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CORRELATION BETWEEN THE IONIZATION POTENTIALS OF TRANSITION METAL COMPLEXES AND OF THE CORRESPONDING LIGANDS*

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SUMMARY

The ionization potentials (*IP*'s) of several monosubstituted carbonylic complexes of the type $M(CO)_5L$, $Fe(CO)_4L$ and $Co(CO)_2NOL$ (M = Cr, Mo and W; $L = PX_3$ or CNR) together with the corresponding phosphinic and isonitrilic ligand *IP*'s, were measured. Good linear correlations were found between the complex and ligand *IP*'s for all the examined series. The slopes of the correlation lines for the phosphinic complexes are very near each other, reflecting the fact that what is in common along the five studied series, is a ligand with a phosphor donor atom. The slope of the correlation line for $Mo(CO)_5CNR$ complexes is much lower and reversed in sign with respect to that for the corresponding phosphinic complexes. The unsubstituted complexes give, in all the cases reported, points well outside the corresponding correlation lines. The results are discussed in terms of the nature of the last occupied molecular orbital in these complexes, which appears to be mainly localized to the metal–ligand M–L bond. The influence of the substituent ligands on the charge distribution to this bond is examined.

INTRODUCTION

A number of semi-empirical correlations between physicochemical properties of zerovalent complexes of transition metals and of substituent ligands were recently reported[1-3]. In determining these correlations different structural parameters—mainly σ-donor and π-accepting ability and polarizability—of the ligands seem to be competitive. Very often these parameters are, however, not easily discriminated each other, as it occurs, *e.g.*, for correlations involving rate constants of ligand substitution or exchange reactions, or ν(CO) and ν(NO) stretching frequencies of series of complexes.

From this point of view, particularly promising appears to be the previously initiated[4,5] study on the ionization potentials (*IP*'s) of monosubstituted tetra- and hexacoordinated complexes, respectively of the type $M(CO)_x(NO)_yL$ and $M(CO)_5L$, and of the corresponding ligands L. The preceding indications suggested that the

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* The present material was partially presented at the 4th Int. Mass Spectrometry Conference, Berlin, Sept. 25, 1967.

IP's of the complexes, at least within series of ligands structurally related and with the same or similar ligand donor atoms, were essentially correlated to the global donor ability of the ligands, *i.e.*, to a property involving both their σ-donor ability and polarizability; the π-accepting ability of the ligands should be on this regard less important. Such global ligand property should be correctly measured to a first approximation, by the experimental ligand *IP*, clearly under the limitation that it always refers to electron detachment from the localized ligand molecular orbital used to form the σ-bond with the central metal atom.

In order to find out possibly a quantitative connection between these two properties, the *IP*'s of seven series of substituted carbonyl complexes and of the corresponding ligands L were measured.

RESULTS AND DISCUSSION

Fig. 1 and Table 1 show that the *IP* of monosubstituted Cr, Mo and W complexes with phosphinic ligands is linearly related to the *IP*★ of the phosphinic ligand itself. The *IP* of the complex is therefore correlated to a quantity which should be in fact a measure of the global donor ability of the PX_3 ligand, including its inductive, mesomeric and polarizability effects (see below). In particular the plots of Fig. 1 show that increasing the ligand donor ability (*i.e.*, decreasing its *IP*) the *IP* of the complex is lowered. On the other side for the various hetero-ligands here studied, their augmented donor capacity is not balanced by an increase of the π-acceptor capacity of the ligand itself. As a consequence the charge density at the

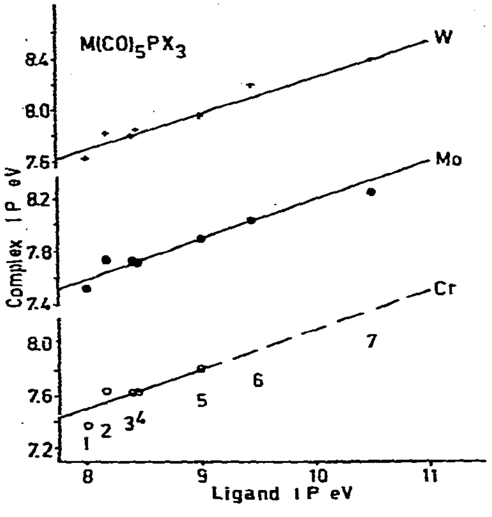

Fig. 1. Plots of complex *IP* *vs.* ligand *IP* for hexacoordinated complexes. The numbering of the ligands refers to Table 1.

★ It was used this property instead of the ligand basicity[6] also because this last property, being measured in solution, is heavily affected by solvation and similar effects which make it poorly comparable with the *IP*★.

TABLE 1

IONIZATION POTENTIALS OF HEXACOORDINATED COMPLEXES (eV)

L No.	L Type	$Cr(CO)_5L$	$Mo(CO)_5L$	$W(CO)_5L$
1	$P(C_4H_9)_3$	7.37	7.51	7.63
2	$P(C_2H_5)_3$	7.63	7.73	7.82
3	$P(OC_2H_5)_3$	7.62[a]	7.72[a]	7.80[a]
4	$P(OC_4H_9)_3$	7.63	7.71	7.85
5	$P(OCH_3)_3$	7.80[a]	7.89[a]	7.96[a]
6	$PCl_2C_6H_5$		8.03	8.20
7	PCl_3		8.25[a]	8.50
8	CO	8.18[b]	8.30[b]	8.46[b]

[a] Ref. 5. [b] Ref. 7.

central metal is increased, causing there a higher electron availability and a lowering of the energy needed to detach an electron from that point. This agrees with the previous suggestion[7] that the molecular orbital involved in the ionization process of the complex be one having a remarkable metal character.

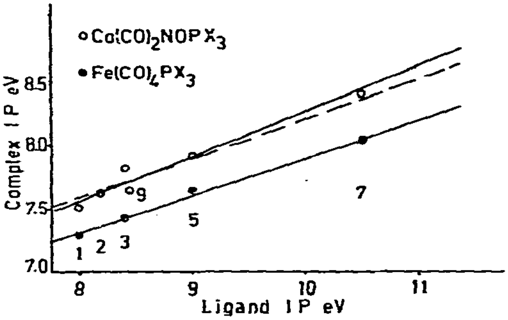

Fig. 2. Plots of complex *IP vs.* ligand *IP* for tetra- and pentacoordinated complexes. The numbering of the ligands refers to Table 2; the dashed line to the $Mo(CO)_5PX_3$ complexes as from Fig. 1.

TABLE 2

IONIZATION POTENTIALS OF TETRA- AND PENTA-COORDINATED COMPLEXES (eV)

L No[a]	L Type	$Fe(CO)_4L$	$Fe(CO)(NO)_2L$	$Co(CO)_2NOL$
1	$P(C_4H_9)_3$	7.29		7.51
2	$P(C_2H_5)_3$			7.62
3	$P(OC_2H_5)_3$	7.43	7.50[b]	7.82
9	$P(iso\text{-}OC_3H_7)_3$			7.64
4	$P(OC_4H_9)_3$		7.52	
5	$P(OCH_3)_3$	7.65	7.66	7.92
7	PCl_3	8.05		8.40[b]
8	CO	8.14[c]	8.45[b]	8.75[b]

[a] The numbering of the ligands is that of Table 1. [b] Ref. 4. [c] Ref. 7.

Another relevant feature of this correlation is that the point for the CO ligand deviates very much from the phosphine line. This seems to be connected to the variation of the donor atom[5] and will be discussed below. It is also noteworthy from Fig. 1 that the correlation lines for the three series of hexacoordinated complexes show nearly the same slope. This indicates that for a given ligand (same row in Table 1) the *IP* of the complex decreases in the order W > Mo > Cr, retaining the same sensitivity to a change of the central metal atom as previously observed[5] for the hexacarbonyls.

An extention of this study to monosubstituted complexes of different type of coordination gave similar results for the *IP*'s (see Table 2) of complexes like $Fe(CO)_4L$, $Co(CO)_2NOL$ and $Fe(CO)(NO)_2L$ when plotted (see Fig. 2) against the *IP*'s of the corresponding phosphinic ligands. For comparison the correlation line (dashed line) for $Mo(CO)_5L$ has been reported. Even in these cases the unsubstituted carbonyls $Co(CO)_3NO$ and $Fe(CO)_5$ deviate remarkably from the corresponding correlation line. It can be observed that

(*a*) the line for the $Co(CO)_2NOPX_3$ series has a slope very near to that for the hexacoordinated complexes, perhaps slightly higher than for the $Mo(CO)_5PX_3$ and $Fe(CO)_4PX_3$ ones;

(*b*) the $Co(CO)_2NOL$ *IP*'s are lowered with respect to the $Co(CO)_3NO$ one more than the $M(CO)_5L$ *IP*'s as compared to the corresponding $M(CO)_6$ ones.

These effects, even if the first one lies near the limits of the experimental accuracy, might reflect the fact that in the tetracoordinated complexes the perturbation from the hetero-ligand spreads out on a smaller number of metal–ligand bonds.

The fact that the slopes for all the diagrams concerning the examined series of complexes turn out to be very near each other, can be connected with the fact that along the five series of complexes above reported, what is in common is a ligand with a phosphor donor atom. This suggests to explain the results in a slightly more precise way. In particular, there is evidence for the ejected electron to pertain to an orbital with metallic character (see above) and to which contributes a phosphinic ligand orbital too. In every substituted complex it is as if the "extraction point" would shift by changing the phosphinic ligand L, always remaining on an orbital mainly localized on the M–L bond. Such a shift clearly should reflect a parallel shift of the electron distribution to the M–L bond.

In agreement with the above argument are the data reported in Fig. 3 and Table 3, regarding the calculated *IP*'s of several disubstituted $Mo(CO)_4LL'$ complexes. The semiempirical method of calculation employed had been tested[8] as to its reliability, so that also in the lack of experimental data, calculated plots like those of Fig. 3 anyway should be useful for the aim of the present discussion.

The $Mo(CO)_4PCl_3L$ line shows the same slope as the $Mo(CO)_5L$ one. This means that the PCl_3 substitution shifts by a definite amount the charge distribution at the Mo–L bond (L = phosphine with lower *IP*), which remains the "extraction point" in the ionization process. In the case of $Mo(CO)_4P(C_4H_9)_3L$, since $P(C_4H_9)_3$ is the phosphine with the lowest *IP* among the used ligands, the *IP* of the complex changes very little along the series. Accordingly the "extraction point" should be considered to remain now localized on the $Mo-P(C_4H_9)_3$ bond, the influence of the second phosphinic ligand L being only indirect. This point of view seems to be supported by the fact that the $Mo(CO)_4P(OCH_3)_3L$ *IP*'s increase with a given slope

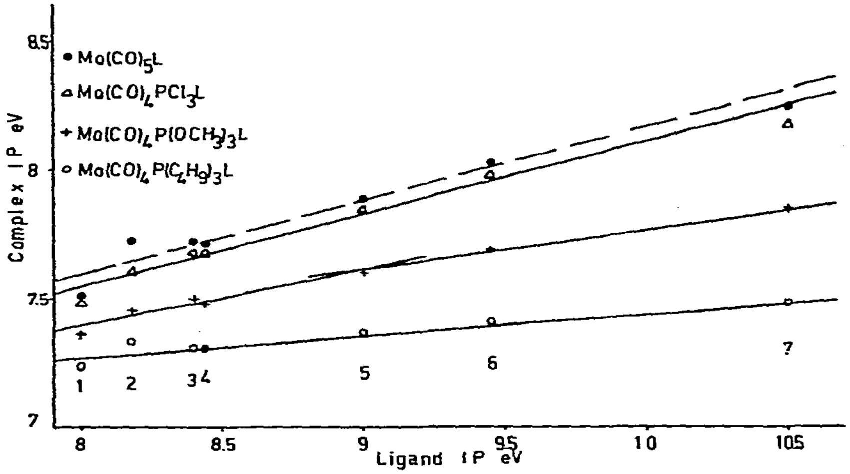

Fig. 3. Plots of calculated *IP* for Mo(CO)$_4$LL′ complexes *vs.* ligand *IP*. The dashed line refers to experimental values for Mo(CO)$_5$PX$_3$ complexes as from Fig. 1.

TABLE 3

CALCULATED IONIZATION POTENTIALS OF M(CO)$_4$LL′ COMPLEXES (eV)

L′ No.	L′ Type	Mo(CO)$_4$P(C$_4$H$_9$)$_3$L′	Mo(CO)$_4$P(OCH$_3$)$_3$L′	Mo(CO)$_4$PCl$_3$L′
1	P(C$_4$H$_9$)$_3$	7.23	7.36	7.48
2	P(C$_2$H$_5$)$_3$	7.33	7.45	7.61
3	P(OC$_2$H$_5$)$_3$	7.30	7.50	7.68
4	P(OC$_4$H$_9$)$_3$	7.30	7.48	7.68
5	P(OCH$_3$)$_3$	7.36	7.60 (7.54)[a]	7.85
6	PCl$_2$C$_6$H$_5$	7.40	7.69	7.98
7	PCl$_3$	7.48	7.85	8.18

[a] Experimental value (see Ref. 8).

on going from Mo(CO)$_4$P(OCH$_3$)$_3$P(C$_4$H$_9$)$_3$ to Mo(CO)$_4$[P(OCH$_3$)$_3$]$_2$. From the last complex to Mo(CO)$_4$P(OCH$_3$)$_3$PCl$_3$ the slope of the correlation line becomes smaller and approaches the one for Mo(CO)$_4$P(C$_4$H$_9$)$_3$L.

Data so far available in this laboratory are giving evidence that different kinds of ligands (as isonitriles or nitrogen-bonded ligands) show, like carbon monoxide, points well outside the phosphine's line. In particular the correlation line for Mo(CO)$_5$CNR complexes (see Fig. 4 and Table 4) has a slope much lower and reversed in sign with respect to that for the corresponding phosphinic complexes. This trend should be connected to the fact that the *IP*'s of these ligands (see Table 4) do not refer to ionization from the isonitrilic carbon. Assuming that the ionization process of the ligand involves now the π system of the CN group, as lower is the experimental *IP*, as higher should be the *IP* regarding electron removal from the carbon lone pair. It follows that actually the *IP* of the isonitrilic complexes should increase with the *IP* related to the σ donor orbital on the isonitrilic carbon.

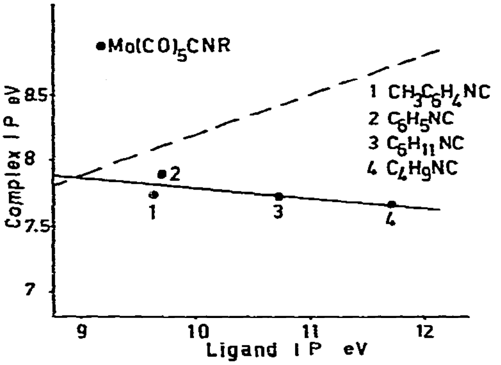

Fig. 4. Plots of complex *IP* *vs*. ligand *IP* for isonitrilic complexes. The dashed line refers to the $Mo(CO)_5PX_3$ complexes as from Fig. 1.

TABLE 4

IONIZATION POTENTIALS OF ISONITRILIC COMPLEXES (eV)

L		$Cr(CO)_5L$	$Mo(CO)_5L$	$W(CO)_5L$	*IP* of L
No.	Type				
1	$CH_3C_6H_4NC$		7.73		9.63
2	C_6H_5NC		7.88[a]	8.03[a]	9.70
3	$C_6H_{11}NC$	7.62[a]	7.72[a]	7.75[a]	10.72
4	C_4H_9NC		7.65	7.60	11.71
5	$C_6H_5CH_2NC$				9.61

[a] Ref. 5.

Therefore the above correlations have the meaning here suggested only if the ligand *IP* measures the energy needed to take out an electron from the ligand lone pair involved in the σ bond with the central metal. This condition, as the correlation reported in Fig. 5 (see also Table 5) puts into light, is well satisfied by phosphinic ligands*.

In any case the study** of $M(CO)_5L$ complexes with arsines, stibines, pyridines, thioethers and similar compounds will be valuable for a better understanding of the effects here discussed. In particular, different slopes might be expected for the various correlation lines, due to the change of the ligand donor atom.

The present results seem to be valuable mainly in connection with the problem of the nature of the last occupied molecular orbital in the organometallic compounds here studied. It appears indeed that, if the nature of the orbital involved in the ionization process of the complex is unchanged along a given series, the *IP*'s of the complexes are linearly correlated with the *IP*'s of the corresponding ligands. This explains why,

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* The *IP*'s of these ligands appear from Fig. 5 to be largely determined by partially mesomeric effects, mainly measured by the $\Sigma\sigma_p^+$ [9,10] of the substituents. Other factors certainly play their role (the correlation between the *IP*'s of aliphatic phosphines and their $\Sigma\sigma^*$ is good), but it is possible in most cases to estimate the *IP* of a given phosphine within about ±0.5 eV once known the $\Sigma\sigma_p^+$. The phosphinic basicity, when measured in solution, is mainly determined instead by the $\Sigma\sigma^*$[6].

** Work in progress in this laboratory.

e.g., the $M(CO)_6$, $Fe(CO)_5$ and $Co(CO)_3NO$ complexes so as the $M(CO)_5Py$ one*, do fall outside the phosphine line; in these molecules the ionization process does not involve any more contribution from a phosphinic ligand orbital.

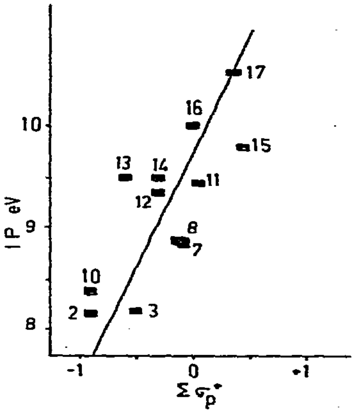

Fig. 5. Ionization potentials of phosphine ligands *vs.* Brown's $\Sigma\sigma_p^+$. The numbering of the ligands is the one reported in Table 5. The literature figures reported in Table 5 were lowered by 0.2 eV when plotted in this diagram, for sake of consistency with our values.

TABLE 5

IONIZATION POTENTIALS OF PHOSPHINES (eV)

Phosphine		Present work	Ref. 11	Ref. 12
No.	Type			
1	$P(C_4H_9)_3$	8.00		
2	$P(C_2H_5)_3$	8.18	8.27	
3	$P(C_6H_5)_3$	8.2		
4	$P(OC_2H_5)_3$	8.40[a]	8.63	
5	$P(OC_4H_9)_3$	8.44		
6	$P(iso\text{-}OC_3H_7)_3$	8.46		
7	$P(C_6H_5)_2Br$	8.72		
8	$P(C_6H_5)_2Cl$	8.75		
9	$P(OCH_3)_3$	9.00	8.82	
10	$P(CH_3)_3$		8.60	9.20
11	$PC_6H_5Cl_2$	9.45		
12	$PH_2C_2H_5$		9.54	
13	$PH(CH_3)_2$			9.7
14	PH_2CH_3		9.72	
15	PBr_3		10.0	
16	PH_3		10.2	10.3
17	PCl_3	10.50[a]	10.75	10.6
18	PF_3		13.00	

[a] Ref. 4.

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* The *IP* for $W(CO)_5Py$ is 7.6±0.2 eV (for Py, $IP=9.8$ eV).

EXPERIMENTAL

The measurements were performed with an Atlas CH4 Mass Spectrometer. The *IP*'s were evaluated by Honig's method[13], the reproducibility being within ±0.05 eV. The samples were prepared following general literature methods (see, *e.g.*[14,15]). The $Fe(CO)_4L$ complexes were obtained, under nitrogen, by sun light irradiation of a mixture of ligand L and excess $Fe(CO)_5$. The Co and Fe derivatives were maintained in the mass spectrometer the minimum time for the measurements, for these two series of compounds having been noticed rather relevant thermal decomposition phenomena. Sometimes inert gas and/or air were introduced together with the sample in order to keep such phenomena to a lower level[16]. For the other experimental details see[4].

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