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Notes

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Reaction of Small Molecules with Low-Valent Metal Complexes: Addition or Oxidative Addition?

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Oxidative-addition reactions of the type

$$ML_m + XY \rightarrow MXYL_m$$

are those in which both the coordination number and formal oxidation state of the metal are raised by two units.[1] It has, however, been acknowledged for some time that certain reactions of this type are not oxidative in character,[2] and addition reactions of even a reductive nature have been observed.[3] The ambiguity attached to the term "oxidative addition" has been an active point of discussion recently.[3,4]

On the basis of the deformation hypothesis it was realized that activation parameters obtained from kinetic studies would not be of any use in distinguishing between addition and oxidative-addition reactions.[5]

A few techniques have been employed to determine the extent of metal-to-ligand or ligand-to-metal charge transfer. Vaska has utilized the very sensitive changes in the carbonyl stretching frequency to probe the extent of metal-to-ligand charge transfer in reactions of $[MCl(CO)(PPh_3)_2]$ (M = Ir or Rh) with addenda molecules.[6] Other researchers have used ^{13}C NMR spectra of metal olefin complexes as an estimate of the electron density on the metal.[3,7] An obvious technique for determining the charge distribution in molecules seems to be X-ray photoelectron spectroscopy (XPS), and correlations between oxidation state and electron binding energies have been demonstrated for a number of systems.[8]

We have decided to investigate the redox character of the reactions

$$[Ir(phen)(cod)]^+ + XY \rightarrow [Ir(phen)(cod)XY]^+ \tag{1}$$

$$[Ir(phen)(cod)]^+ + L \rightarrow [Ir(phen)(cod)L]^+ \tag{2}$$

(where XY = O_2, Cl_2, HCl, or CH_3I, L = PPh_3, SCN^-, I^-, C_2H_4, or C_2H_2, phen = 1, 10-phenanthroline, and cod = cycloocta-1,5-diene) by means of XPS. Since the activation of dioxygen by transition-metal complexes is a controversial subject,[9] we have also determined the binding energies of the dioxygen adducts of $[Ir(dppe)_2]Cl$ [dppe = 1,2-(diphenylphosphino)ethane], $[IrCl(PPh_3)_3]$, and $[IrCl(CO)(PPh_3)_2]$. All the starting complexes and adducts have been prepared by literature methods.[10]

The XPS spectra were recorded on a Kratos ES200B photoelectron spectrometer using unmonochromatized Al $K\alpha_{1,2}$ radiation (1486.6 eV) under ca. 10^{-8} torr. For the minimization of charging effects, thin-film samples of the compounds were precipitated from dichloromethane solutions onto gold. This allowed ready detection of the gold $4f_{5/2}$ peak (87.0 eV), which was used as a binding energy reference. The use of the C(1s) level as a reference[11] was abandoned, as the origin of this signal is uncertain. Measurements made at both room temperature and −170 °C agreed within ±0.3 eV, and no time-dependent changes were observed in the spectra. Thus we believe that photochemical reduction, which has been observed in certain systems,[12] is absent in this study. In all cases the resolution of the $Au(4f_{7/2})$–$Au(4f_{5/2})$ and $Ir(4f_{7/2})$–$Ir(4f_{5/2})$ peaks was good; Table I contains the $Ir(4f_{7/2})$ and Ir $(4f_{5/2})$ binding energies of the complexes studied. The larger Ir(4f) spin–orbit splitting (3.3–3.5 eV) compared to that in previous work[11,13] (2.7–3.3 eV) can be attributed to differences in instrumental resolution. From the magnitude of the Ir(4f) binding energies recorded in this table, two groups of complexes can be distinguished, according to the reaction by which they are formed, with larger binding energies for products of reaction 1. Assuming oxidation states of +1 and +3 for the complexes [Ir(phen)(cod)]Cl and $[Ir(phen)(cod)Cl_2]Cl$, and furthermore that the binding energy can be considered a linear function of the electron density on the metal,[8] we assigned relative oxidation numbers to the products of reaction 1 (Table II). For the complexes $[Ir(dppe)_2]Cl$, $[IrCl(CO)(PPh_3)_2]$, and $[IrCl(PPh_3)_3]$ we have assumed that the chlorine adducts have an increasing binding energy of 1.9 eV over that of the starting complexes, as was the case for $[Ir(phen)(cod)Cl_2]Cl$. These data are given in Table II. The metal core binding energies depend, mainly, on the atomic charge, the geometry of the complex, and the nature of the ligands attached to the complex; however, since we worked with closely related compounds, we believe the observed binding energy changes are dominated by electron-transfer effects.

Studies on [Ir(phen)(cod)XY]Cl Where XY = Cl_2, HCl, or CH_3I[9]

The addition reactions of these XY molecules with low-valent metal complexes are generally accepted to be oxidative in nature. From Tables I and II a considerable metal-to-ligand charge transfer is indicated; moreover, it is not a stepwise increase but rather a gradual change, as was noted before.[6,14] This once again illustrates that oxidation number is a formalism that cannot be applied in an absolute way.[15] Interestingly, the relative oxidation numbers obtained are in reasonable agreement with those obtained by Vaska for $[IrCl(CO)(PPh_3)_2]$ using the ν_{CO} IR stretching frequencies as indicators[6] (Table II).

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Table I. Binding Energies (eV) of Some Iridium Complexes (±0.3 eV)

substrate	Ir($4f_{5/2}$)	Ir($4f_{7/2}$)	reaction 2	Ir($4f_{5/2}$)	Ir($4f_{7/2}$)	reaction 1	Ir($4f_{5/2}$)	Ir($4f_{7/2}$)
[Ir(phen)(cod)]Cl	66.3	62.7	[Ir(phen)(cod)PPh_3]Cl	65.8	62.3	[Ir(phen)(cod)Cl_2]PF_6	68.2	64.8
			[Ir(phen)(cod)SCN]	65.6	62.3	[Ir(phen)(cod)HCl]PF_6	68.2	64.7
			[Ir(phen)(cod)I]	65.7	62.4	[Ir(phen)(cod)CH_3I]I	67.8	64.2
			[Ir(phen)(cod)(C_2H_2)]Cl	66.3	62.8	[Ir(phen)(cod)O_2]I	66.8	63.5
			[Ir(phen)(cod)(C_2H_4)]Cl	66.4	63.0			
[Ir(dppe)$_2$]Cl	67.0	63.5	[Ir(dppe)$_2$CO]Cl	66.6	63.1	[Ir(dppe)$_2O_2$]Cl	67.3	63.9
[IrCl(CO)(PPh_3)$_2$]	66.2	62.6				[IrCl(CO)(PPh_3)$_2O_2$]	67.4	64.0
[IrCl(PPh_3)$_3$]	65.8	62.5				[IrCl(PPh_3)$_3O_2$]	66.7	63.3

Table II. Relative Oxidation Number (ON) of Products of Iridium(I) Complex Reactions with Various Small Molecules

substrate	L or XY	ON	ON[a]
[Ir(phen)(cod)]Cl	SCN^-	0.26	
	I^-	0.37	
	PPh_3	0.47	
	C_2H_2	1.00	
	C_2H_4	1.11	
	O_2	1.53	1.89
	CH_3I	2.58	2.48
	HCl	3.00	2.46
	Cl_2	3.00	3.00
[Ir(dppe)$_2$]Cl[b]	CO	0.6	
	O_2	1.3	
[IrCl(PPh_3)$_3$][b]	O_2	1.9	
[IrCl(CO)(PPh_3)$_2$][b]	O_2	2.2	1.89

[a] Values obtained by Vaska on the basis of ν_{CO} stretching frequencies for the complex [IrCl(CO)(PPh_3)$_2$]. [b] Values based on the assumption that the Ir(4f) binding energies of the Cl_2 adducts of these complexes will increase by 1.9 eV.

Studies on [Ir(cod)(phen)L]Cl Where L = SCN^-, I^-, PPh_3, C_2H_2, or C_2H_4

The reactions of these L molecules are generally accepted to be simply addition reactions. In contrast to ligands such as $C_2(CN)_4$, $C_2(Ph)_2$, and C_2F_4 where considerable metal-to-ligand charge transfer has been noted[6,10] C_2H_2 and C_2H_4 show no net charge transfer in [Ir(phen)(cod)L]Cl (Table II). This can be explained by similar σ-bonding and π-back-bonding effects. However, in the softer [Pt(PPh_3)$_2$(C_2H_4)] complex the oxidation number of platinum was estimated[19] to be +0.8, indicating that this complex has a much greater π-back-bonding component.

As expected, a considerable ligand-to-metal charge transfer is obtained for L = SCN^-, I^-, PPh_3, and CO. Kinetically PPh_3 and CO are better nucleophiles[16] than SCN^- and I^-, but their ability to participate in π back-bonding is most probably the reason why iridium oxidation numbers of 0.47 and 0.6 are obtained for PPh_3 and CO as compared to the 0.26 and 0.37 values for SCN^- and I^-, respectively.

Studies on Dioxygen Uptake

There has been much speculation as to whether this reaction should be considered an addition or oxidative-addition reaction.[9] From Table II it is clear that some charge has been accepted by the dioxygen molecule for all the complexes studied.

The kinetics and mechanism of the reaction Ir(phen)(cod)X + O_2 → [Ir(phen)(cod)O_2]$^+$ + X^- where X = Cl, I, or SCN have been published recently.[17] For X = Cl the starting complex is four-coordinate (Cl being the counterion) while I^- and SCN^- bind reversibly to form five-coordinate complexes.[10a] It was found that the rate of oxygen uptake increases in the series $Cl^- \ll I^- < SCN^-$. As is shown in Table II, SCN^- and I^- donate electrons into the iridium center, making it a much better nucleophile, and therefore enhancing the rates of oxidative additions toward electrophiles.[17-19] This is therefore in keeping with dioxygen adding oxidatively to metal complexes.

The data presented here and elsewhere[20] clearly show that a distinction between oxidation states is often very difficult to make since a range of binding energies can be found within a formal oxidative state.

Registry No. [Ir(phen)(cod)]Cl, 53522-11-5; [Ir(dppe)$_2$]Cl, 15390-38-2; IrCl(CO)(PPh_3)$_2$, 14871-41-1; IrCl(PPh_3)$_3$, 16070-58-9; [Ir(phen)(cod)PPh_3]Cl, 80263-33-8; Ir(phen)(cod)SCN, 66779-01-9; Ir(phen)(cod)I, 41392-85-2; [Ir(phen)(cod)(C_2H_2)]Cl, 80263-34-9; [Ir(phen)(cod)(C_2H_4)]Cl, 80263-35-0; [Ir(dppe)$_2$CO]Cl, 15308-58-4; [Ir(phen)(cod)Cl_2]PF_6, 80263-37-2; [Ir(phen)(cod)HCl]PF_6, 53522-18-2; [Ir(phen)(cod)CH_3I]I, 80287-61-2; [Ir(phen)(cod)O_2]I, 80263-38-3; [Ir(dppe)$_2O_2$]Cl, 19214-64-3; IrCl(CO)(PPh_3)$_2O_2$, 15187-10-7; IrCl(PPh_3)$_3O_2$, 42583-98-2.

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Enthalpy of the Oxidative Addition of Tetrachloro-1,2-benzoquinone to {M[*cis*-$(C_6H_5)_2PCHCHP(C_6H_5)_2$]$_2$}$BF_4$ (M = Cobalt, Rhodium, or Iridium)

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We wish to report a study of the enthalpy change for oxidative-addition reactions at square-planar cobalt(I), rhodium(I), and iridium(I) centers. Direct comparison of the three metals in this way is rarely possible due to differing structural requirements. the oxidative-addition reaction is found as a step in numerous catalytic and stoichiometric reactions of four-coordinate, d^8 complexes.[1-3] This has been studied in some detail for rhodium(I) and iridium(I) since numerous four-coordinate complexes have been synthesized and conveniently handled.[4,5] For cobalt(I), a coordination number of five is most favorable and oxidative addition requires prior dissociation of one ligand.[4] Hence direct comparison of reactivity of the three metals is not usually possible.

The synthesis of CoCl(PPh_3)$_3$ has been reported,[6] but this complex is presumed to be tetrahedral and lacks the reactivity of square-planar cobalt(I) or of analogous rhodium(I) and

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