Journal of Organometallic Chemistry, 199 (1980) 99—106
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

OXIDATIVE VERSUS REDUCTIVE ADDITIONS: A ^{13}C NMR STUDY OF H_2, HX (X = Cl, Br, OR I), AND Cl_2 ADDITIONS TO SOME IRIDIUM(I) COMPLEXES

ROBERT H. CRABTREE * and JENNIFER M. QUIRK
Yale Department of Chemistry, 225 Prospect Street, P.O. Box 6666, New Haven, CT 06511 (U.S.A.)

(Received April 16th, 1980)

Summary

The ^{13}C NMR spectra of a number of iridium complexes and of their adducts with H_2, HX, and Cl_2 (X = Cl, Br, I) are used to estimate the redox character of these additions. Rather than having the oxidative character expected, H_2 addition seems to be reductive. HX and Cl_2 additions are oxidative. Some of these complexes appear to have Lewis acid, rather than the expected Lewis base character.

Additions of the type shown in eq. 1 have been termed "oxidative" additions

$$L_nM + XY \rightarrow L_nMXY \tag{1}$$

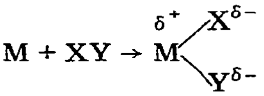
$$(\text{e.g. } X = Y = H, Cl, Br, I, O; X = CH_3, Ar; Y = Cl, Br, I)$$

since the pioneering investigations of Vaska [1]. He showed that $IrCl(CO)(PPh_3)_2$ (I) undergoes many such additions, for which the adducts can be isolated and studied. The presence of a CO in each species allows an estimate to be made of the oxidative character of the addition, since the C—O infrared stretching frequency is sensitive to the electron density at the metal.

By assigning notional oxidation states of 3.0 to the Cl_2 adduct $IrCl_3(CO)(PPh_3)_2$ and 1.0 to the starting complex I, Vaska was able to obtain reasonable estimates of the relative oxidising tendencies of a variety of addenda: Cl_2 (3.0) > Br_2 (2.95) > I_2 (2.85) > MeI (2.48) > HCl (2.46) > H_2 (2.24) > O_2 (1.89) (estimated oxidation state of adduct in brackets).

A detailed thermodynamic study [1b] reinforced these conclusions by showing that K_{eq} for H_2 addition increases sharply with increasing ligand basicity in a series of complexes analogous to I. All these additions therefore seem to be oxidative, the metal acting as a net source of negative charge (eq. 2).

0022—328X/80/0000—0000/$02.25, © Elsevier Sequoia S.A.



$$M + XY \rightarrow M^{\delta+}\begin{matrix} X^{\delta-} \\ Y^{\delta-} \end{matrix} \tag{2}$$

Chatt and Butter [2] extended these ideas by showing that $Rh(dpe)_2^+$ (dpe = 1,2-diphenylphosphinoethane) is inert towards H_2 addition, but that substitution of the more strongly electron-donating dmpe ligand (dmpe = 1,2-dimethylphosphinoethane) activates the metal towards addition. This is consistent both with the idea that the addition has oxidative character, since more strongly donating ligands should indeed drive the equilibrium of eq. 2 ($X = Y = H$) to the right, and with the commonly held view that low valent transition metal complexes have Lewis base character [1b,3].

We now report evidence showing that additions having reductive character are also possible.

Results and discussion

We have recently reported the reactions of hydrogen with a series of complexes, $[Ir(cod)L_2]PF_6$ (cod = 1,5-cyclooctadiene, L = phosphine, amine, or olefin); these complexes, in non-coordinating solvents, are also precursors for hydrogenation catalysts of exceptional activity, especially for the reduction of hindered olefins. We found that hydrogen addition at −80°C proceeded quantitatively to give adducts stable enough to be completely characterised, and in some cases, even to be isolated.

$$[Ir(cod)L_2]^+ \xrightarrow[-80^\circ C]{H_2} cis\text{-}[IrH_2(cod)L_2]^+ \tag{3}$$

On warming, H_2 can be lost or the coordinated olefin can undergo hydrogenation, in which case a variety of further reactions can also occur.

Unexpectedly, the hydrogen addition process for these 16-electron systems is inhibited by relatively electron-donor ligands such as pyridine (py), Cl^-, Br^-, or I^-, (e.g. $Ir(cod)py_2^+$) but occurs readily with relatively electron-accepting ligands such as $Palkyl_3$, $Paryl_3$ or olefin. This result is contrary to the accepted view of the addition as oxidative.

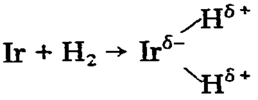
Most, if not all, systems which undergo oxidative addition of H_2, also react with the more oxidising addenda, such as MeI. It was therefore surprising that $[Ir(cod)(PPh_3)_2]^+$ reacts only very slowly with MeI, not to give products of oxidative addition, but via eq. 4.

$$[Ir(cod)(PPh_3)_2]^+ \xrightarrow[MeOH,\ 6\ h]{MeI} [IrI(cod)PPh_3] + PMePh_3I \tag{4}$$

This reaction presumably arises because, as is known from other studies [4], phosphine dissociates slightly from these complexes. Interestingly, Usòn, Oro, and Fernandez [5] have recently observed normal MeI addition to the more electron-rich $[Ir(cod)(P\{p\text{-tolyl}\}_3)_2]BF_4$.

Our working hypothesis [4b] was that these cationic iridium complexes tend to attract negative charge in their reactions (Lewis acid behavior), rather than, as in the many well-studied electron-rich systems discussed above, disperse it

(Lewis base). The addition of hydrogen would then be a reductive (eq. 5), rather than an oxidative (eq. 2, $X = Y = H$) process.



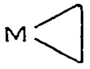
$$\mathrm{Ir} + \mathrm{H_2} \rightarrow \mathrm{Ir}^{\delta-}\!\begin{matrix}\diagup \mathrm{H}^{\delta+}\\ \diagdown \mathrm{H}^{\delta+}\end{matrix} \qquad (5)$$

The fact that the Pauling electronegativities of Ir (2.2) and H (2.1) are comparable, is consistent with this picture. Additions of H_2 to complexes of cobalt (1.9) or manganese (1.55), for example, would be more likely to be oxidative. The positive charge and the presence of the electron-withdrawing olefinic ligands in these iridium complexes seem to be significant factors, since H_2 addition to Vaska's complex (I) is indeed oxidative.

In order to test this idea we have compared the ^{13}C NMR spectra of a number of cationic iridium-olefin complexes and their H_2, HX ($X = Cl, Br, I$) and in one case, Cl_2 adducts.

An olefin attached to a metal seems to be able to act as a probe of the electron density at the metal [6], just as did the CO ligand in Vaska's work [1]. The metal—olefin bond can be usefully considered [7] as having contributions from two limiting structures A and B:

(A)

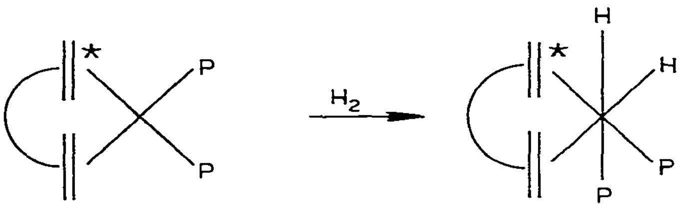


(B)

In A, the olefin acts as a conventional 2*e* donor L-type ligand. This model is appropriate for relatively electron-poor metal centers; the coordinated ligand resembles the free olefin. In B, the olefin acts as an X_2 (2×1 electron) "dialkyl" ligand. This model seems to be most appropriate for electron-rich metal centers.

Recent work has shown [6] that ^{13}C NMR spectroscopy provides a good estimate of the relative contributions of L or X_2 character in a metal-olefin system, especially when comparisons can be made between members of the same series. Both $\delta(^{13}C)$ and $^{1}J(^{13}C, H)$ for the vinylic carbons of olefin ligands have been studied in this regard. The chemical shift seems to be a better measure of metallacyclopropane character and π back-bonding than the coupling constant [6].

The values of the chemical shift differences on addition ($\Delta\delta$) are shown in Table 1. These were calculated from the full ^{13}C NMR results shown in Table 2. Not all the adducts have the same stereochemistry, a fact which would make these differences hard to compare if we took no special precautions. We therefore decided to calculate $\Delta\delta$ from chemical shift changes in the vinyl carbons only of olefinic groups which remain *trans* to the same ligand both in the starting complex and in the adduct. For example, in eq. 6, only one of the two



(6)

TABLE 1

^{13}C NMR SHIFTS OF cod VINYLIC CARBONS IN REDUCTIVE AND OXIDATIVE {3.2}[a] ADDITIONS TO SOME IRIDIUM(I) COMPLEXES

Complex[b]	Addendum	Δδ	Redox character	Δ_{os}[c]
$Ir(cod)_2^+$	H_2	−20.3[d]	Red	−1.1[d]
$Ir(cod)(PPh_3)_2^+$	H_2	−3.3	Red	−0.2
$Ir(cod)(PMePh_2)_2^+$	H_2	−3.7	Red	−0.2
$Ir(cod)(PMePh_2)_2^+$	HI	+10.1	Ox	+0.6
$Ir(cod)(PMePh_2)_2^+$	HBr	+10.1	Ox	+0.6
$Ir(cod)(PMePh_2)_2^+$	HCl	+10.8	Ox	+0.6
$IrI(cod)PPh_3$	HI	+11.8	Ox	+0.7
$IrBr(cod)PPh_3$	HBr	+14.6	Ox	+0.8
$IrCl(cod)PPh_3$	HCl	+15.0	Ox	+0.8
IrCl(cod)py[e]	Cl_2	+35.6	Ox	+2.0[f]

[a] 3 center, 2 electron addition (see ref. 14), a momenclature that does not make the presumption of oxidative character. [b] cod = 1,5-cyclooctadiene. [c] Oxidation state change, based on Δ_{os} for Cl_2 addition being 2.0 (see text). [d] This value is probably affected by factors other than the reductive character of the addition (see text). [e] py = pyridine. [f] By definition (see text).

coordinated olefin groups (marked with an asterisk) remains *trans* to phosphorus throughout. This group can be identified because it shows characteristic $^2J_{trans}(^{13}C, P)$ coupling [8].

The results of Table 1, calculated as discussed above, support the idea that

TABLE 2

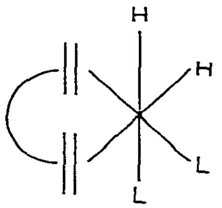
FULL ^{13}C NMR DATA FOR THE IRIDIUM COMPLEXES

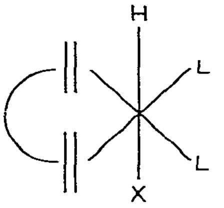
Complex[a]	cod-vinyl	cod-allyl	PMe
$Ir(cod)(PPh_3)_2^+$	86.9c[b]	30.8	—
$Ir(cod)(PMePh_2)_2^+$	86.9c[b]	31.0	—[c]
$Ir(cod)_2^+$	99.5	29.5	—
$IrCl(cod)PPh_3$	93.8 d(14), 53.5	33.3, 29.4	—
$IrBr(cod)PPh_3$	93.1 d(13), 54.2	33.1, 29.7	—
$IrI(cod)PPh_3$	91.6 d(6), 56.5	32.7, 30.4	—
$IrHCl_2(cod)PPh_3$	102.8 d(18), 100.2 d(10), 78.8, 72.2	28—39[a]	—
$IrHBr_2(cod)PPh_3$	101.8 d(20), 100.2 d(12), 79, 72.	27—39[d]	—
$IrHI_2(cod)PPh_3$	97.2 d(12), 94.8 d(18), 79.6, 71.6.	27—38[d]	—
$IrHCl(cod)(PMePh_2)_2^+$	99.0c[b], 96.3c[b]	32.9, 28.8	11.2 d(40)
$IrHBr(cod)(PMePh_2)_2^+$	98.8c[b], 95.1c[b]	32.4, 29.7	12.2 d(44)
$IrHI(cod)(PMePh_2)_2^+$	98.6c[b], 95.4c[b]	31.5, 29.5	12.3 d(41)
$IrH_2(cod)(PPh_3)_2^+$[e]	88.8, 86.6, 84.7, d(15), 82.6 d(5)	25—28	—
$IrH_2(cod)(PMePh_2)_2^+$[e]	89.0, 84.2, 83.6, d(8), 82.9 d(13)	28—32	17.1 d(44), 8.2 d(32)
$IrH_2(cod)_2^+$[e]	99.8, 99.2, 81.2[f], 77.2[f]	22—34	—
$IrCl_3(cod)(py)$	99.3, 100.3	30.1, 30.5	—
IrCl(cod)(py)	64.2[g]	31.3	—

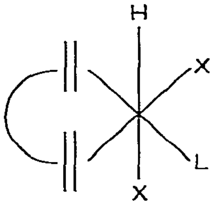
[a] Fluoroborate salt in $CDCl_3$. Data reported as: position with respect to TMS (ppm), multiplicity (c = complex, d = doublet, singlet otherwise), coupling constant (in parentheses Hz). Complexes containing Ph group have appropriate resonances at 127—135 ppm. [b] A distorted "triplet" resonance probably due to virtual coupling ($J \approx 5$ Hz). [c] Not observed, low solubility. [d] Values from ref. 8a. [e] *cis*-isomer. [f] Assigned to olefinic groups *trans* to cod. [g] Fluxional at 25°C, see ref. 4.

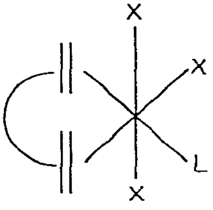
the addition of H_2 to Ir(cod)$_2^+$ (IIa) and Ir(cod)L_2^+ (L = PPh_3, IIb; and $PMePh_2$, IIc) has reductive character. The additions of HX (X = Cl, Br, I) to the cations IIc and to the neutral complexes [IrX(cod)L] (III), in contrast, are moderately oxidising, and the addition of X_2 to [IrX(cod)py] (IV, py = pyridine) is very oxidising.

The stereochemistries that have been determined for these adducts [8,9,10] are shown below; they seem to be completely reliable:





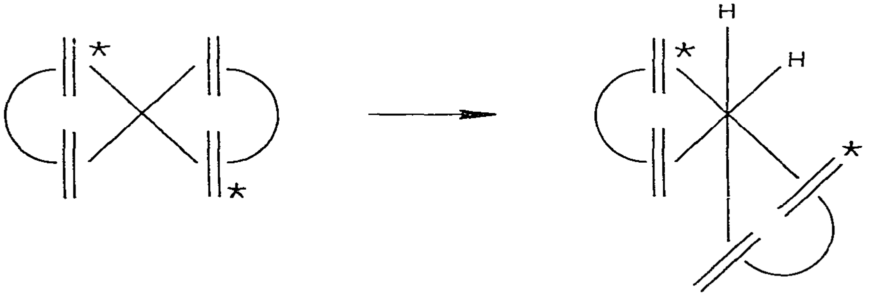




In the final column of Table 1 is shown an approximate estimate of the change in oxidation state (Δ_{os}) during the additions. The addition of Cl_2 to IV was used to calibrate the scale, in a way similar to that used by Vaska [1]: Δ_{os} for this addition was defined as 2.0 ($Ir^{I} \rightarrow Ir^{III}$) and $\Delta\delta$ was assumed to be linearly related to electron-density changes at the metal. The data available [6] suggest this assumption is reasonable, but only further data can test it thoroughly; further work is in progress.

The slightly reductive nature of the addition of H_2 to the two Ir(cod)L_2^+ cations, suggested by the results, seems to us to be real.

The strongly negative $\Delta\delta$ for H_2 addition to Ir(cod)$_2^+$ (IIa) may be misleading. The olefinic groups marked with an asterisk in eq. 7 remain mutually *trans* throughout, but the relative orientation of these groups changes from coplanar (in IIa) to orthogonal (in the adduct). These olefins are therefore competing for electrons in the same metal orbital in IIa but π-bound to different orbitals in the adduct. The stereochemical change alone would be expected to lead to greater metallacyclopropane character in the adduct. Some of the observed $\Delta\delta$ must arise from this effect, although we believe the addition is still reductive. Perhaps the shift averaged over all the olefinic groups ($\Delta\delta_{av}$ −10.2 ppm) is a more appropriate measure of the redox character of the addition in this particular case.



(7)

(IIa)

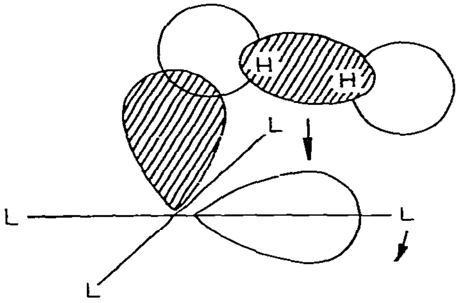
We also hoped to use the shifts we observed [11] for the monoolefin complexes $IrH_2(olefin)_2(PPh_3)_2^+$ (V) and *trans*-$Ir(olefin)_2(PPh_3)_2^+$ to examine the redox character of the addition in this case too. For the ethylene complexes, the olefins are mutually *trans* in the iridium(I) cation but *trans* to H in the adduct, so that $\Delta\delta$ cannot be obtained. In the cases of styrene and cyclooctene, Morris [12] has provided convincing evidence that the adduct is $IrH_2(acetone)(olefin)(PPh_3)_2^+$, not V as we originally suggested; our preliminary NMR assignments [11] will therefore have to be modified.

The additions of HX appear to be oxidative, as expected. The nature of X does not have a great influence, the order of oxidising power being Cl > Br > I. Additions of HX to these complexes seem to be more oxidising in the case of the more electron-rich $IrX(cod)PPh_3$ than the less electron-rich $Ir(cod)(PMePh_2)_2^+$. The redox character therefore depends, as might be expected, on the nature both of the starting complex and of the addendum.

The complexes which contain a planar $codIrL_2^+$ fragment, viz.: $Ir(cod)L_2^+$ and $IrHX(cod)L_2$, show an unusual virtually coupled "triplet" for their vinylic cod carbons (J apparent ≈5 Hz). The complexes *cis*-$[IrH_2(cod)L_2]^+$, in contrast, show no trace of this behavior. We do not as yet understand this difference.

The addition of Cl_2 to IrCl(cod)py appears to be slightly more than twice as oxidative as the HX additions we studied. Preparative or solubility problems prevented a study on Cl_2 adducts of II—III.

In view of the importance of metal Lewis acidity in the overall addition of H_2 to the complexes II, it may also be important in the approach to the transition state. One can imagine the donation of H_2 electrons into the empty $d_{x^2-y^2}$ orbital which lies in the square plane of the complex, being accompanied by back donation from the filled d_{z^2} orbital into the empty σ^* orbitals on H_2. This would lead to an unsymmetrical mode of attack as shown below (filled orbitals shaded), for which a theoretical study might prove interesting:



Other cases of reductive additions

Other examples of reductive additions of H_2 will no doubt be found; they will probably be most numerous among cationic complexes of the more electronegative transition elements (Ru—Pd, Os—Au) containing electron-withdrawing ligands. Additions of the more electropositive addenda, e.g., Li_2 [13] or R_3SnH may be reductive even in the cases of more electropositive transition metals. We have recently suggested [14] a nomenclature scheme for this and other reactions, which does not make the presumption of oxidative character implicit in the term "oxidative" addition (e.g., oxidative and reductive addition would both be 3-center, 2-electron {3,2} additions).

Further implications of the Lewis acidity of these iridium complexes

Other unusual features of the chemistry of these iridium cations can also be understood in terms of their Lewis acidity. For example, neither the diolefin complexes, nor the homogeneous hydrogenation catalysts derived from them, add O_2 or $CHCl_3$ [5]. The metal seems reluctant to engage in reactions having any marked degree of oxidative character.

$[Ir(cod)L_2]^+$ (L = PPh_3 or $PMePh_2$) add HX (X = Cl, Br or I) by an ionic mechanism [8], of a type otherwise unknown: X^- attack, followed by protonation. Here too the complexes seem to act as Lewis acids rather than bases. The positive charge on the complex is not wholly responsible for this behavior since $IrCl(cod)PEtPh_2$ shows the same order of addition [8b]. The cationic complexes do react with X_2, but they only give what seems to be $[IrX_3(cod)L]$ [9], where X = Cl or Br, and a hydrogen iodide adduct $[IrHI_2(cod)PPh_3]$, where X = I and L = PPh_3 [8a]. In the latter case the metal forms the less oxidised HI adduct rather than the more oxidised, and as yet unknown I_2 adduct.

We have recently shown [11] that, in the presence of 3,3-dimethyl-1-butene, $[IrH_2(acetone)_2(PPh_3)_2]^+$ in refluxing 1,2-dichloroethane dehydrogenates cycloalkanes. This is surprising since a species capable of activating CH bonds might have been expected to add to the CH bonds of its own PPh_3 ligands or to the CH or Cl bonds of the solvent. The Lewis acid character of these complexes may kinetically inhibit these additions since they are all oxidising. *ortho*-Metallation might still occur, but be reversible; any addition to the solvent, however, would not be expected to be reversible.

By inhibiting classical reaction pathways of low-valent d^8 complexes, we seem to be able to observe new and unusual chemistry. We are currently extending these studies to cationic complexes of elements neighboring iridium in the Periodic Table.

Experimental

The complexes were prepared by standard methods [4,8,9]. ^{13}C NMR spectra were recorded on Brucker 67.6 MHz and Varian CFT 20 MHz instruments in $CDCl_3$ and at 25°C, except for the unstable H_2 adducts, which were studied at —60°C.

The full results are shown in Table 2.

The reactions of $[Ir(cod)(PPh_3)_2]BF_4$ *with MeI,* CH_2Cl_2, $CHCl_3$ *and* O_2

The title complex (100 mg) was treated with MeI (0.2 ml) in MeOH (20 ml) at room temperature. After 4 h the suspension turned yellow-orange, and solid isolated from the mixture proved to be $[IrI(cod)(PPh_3)]$ (yield ca. 80%), as shown by comparison of its IR and PMR spectra with those of an authentic sample [8,9].

The title complex was recovered unchanged from CH_2Cl_2, or $CHCl_3$ solution after 24 h in air.

Acknowledgements

We thank Drs. George Morris (Warwick) and Luis Oro (Zaragoza) for communicating some of their results, Mr. Peter Demou for generous help in obtaining spectra, the NSF and PRF for funding, and Johnson Matthey Inc. for a loan of part of the iridium.

References

1 (a) L. Vaska, Accounts Chem. Res., 1 (1968) 335; (b) L. Vaska and M.F. Werneke, Trans. N.Y. Acad. Sci., 33 (1971) 70.
2 J. Chatt and S.A. Butter, Chem. Commun., (1967) 501.
3 G. Dolcetti and N.W. Hoffmann, Inorg. Chim. Acta, 9 (1974) 269.
4 (a) R.H. Crabtree and G.E. Morris, J. Organometal. Chem., 135 (1977) 395; (b) R.H. Crabtree, Accounts Chem. Res., 12 (1979) 331.
5 R. Usón, L.A. Oro and M.J. Fernandez, J. Organometal. Chem., 193 (1980) 127.
6 C.A. Tolman, A.D. English and L.E. Manzer, Inorg. Chem., 14 (1975) 2353; P.W. Clark, P. Hamisch and A.J. Jones, Inorg. Chem., 18 (1979) 2067.
7 M.J.S. Dewar and G.P. Ford, J. Amer. Chem. Soc., 101 (1979) 783.
8 (a) R.H. Crabtree, J.M. Quirk, T. Fillebeen-Khan and G.E. Morris, J. Organometal. Chem., 181 (1979) 203; (b) T.V. Ashworth, J.E. Singleton, D.J.A. de Waal, W.J. Louw, E. Singleton and E. van der Stok, J. Chem. Soc., Dalton (1978) 340.
9 R.N. Haszeldine, R.J. Lunt and R.V. Parrish, J. Chem. Soc. A, (1971) 3711.
10 R.H. Crabtree, H. Felkin, T. Fillebeen-Khan and G.E. Morris, J. Organometal. Chem., 168 (1979) 183.
11 R.H. Crabtree, J.M. Mihelcic and J.M. Quirk, J. Amer. Chem. Soc., 101 (1979) 7731.
12 G.E. Morris, personal communication, 1980.
13 K. Jonas, Angew. Chem., Int. Ed., 14 (1975) 752.
14 R.H. Crabtree and G.G. Hlatky, Inorg. Chem., 19 (1980) 572.