Carbonyl complexes of late transition elements: atypical M—CO bonds

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Abstract- The effect of the change of the halide ligand on the chemical , spectroscopic i.r. and NMR data of halo-carbonyl complexes of platinum(II) and palladium(II) has been studied . The results , in conjunction with other peripheral information suggest that the M-CO bond in these complexes has a predominant σ component .

INTRODUCTION

The elements at the end of the transition series forming M-CO bonds are interesting under several respects . The tetracarbonyls of palladium(0) and platinum(0) are assumed to be for all practical purposes intrinsically unstable with respect to their decomposition to metals under the ordinary conditions of temperature and p_{CO} ; in spite of the fact that we are dealing with cations with totally ($Au(I), d^{10}$) or almost completely ($Pd(II), Pt(II), Au(III), d^8$) filled electronic d configurations , acidic and/or electrophilic properties are sometimes displayed (metalation of aromatics by anhydrous gold(III) chloride (ref.1) , high $\tilde{\nu}_{CO}$'s in their halo-carbonyl complexes (ref.2) ;the use of palladium and platinum in metal-mediated organic syntheses (ref.3) and in some important industrial processes (ref.4)).

For these reasons it appeared worthwhile to have a closer consideration of these systems and possibly obtain a better understanding of the properties of metal-CO bond .

SYNTHETIC PROCEDURE

Work carried out in these laboratories on halo-carbonyl complexes of the above mentioned cations had pointed out some unusual features . The research originated from attempts to find suitable conditions to stabilize carbonyl derivatives of platinum in low oxidation states (ref.5) . Although the attempts have been unsuccessful , an important development in this area came from the observation that the chloro-carbonyl complexes of gold(I) (ref.6) and platinum(II) (ref.7) , i.e. $AuCl(CO)$ and $PtCl_2(CO)_2$,respectively , which are extremely reactive towards water , are unreactive towards $SOCl_2$, which,on the contrary , behaves as an oxidizing agent for many other metal carbonyl derivatives . The fortunate combination of nonoxidizing and dehydrating properties of thionyl chloride allowed us to observe several phenomena which otherwise would have presumably escaped our attention . The new finding , combined with the already known (ref.8) reducing properties of CO towards gold(III) led to a simple preparative method for $AuCl(CO)$ consisting of treating (ref.6) the commercially available tetrachloroauric acid with $SOCl_2$ as a reagent and a solvent , and with CO at atmospheric pressure and room temperature or slightly above . The extension of this synthetic procedure to platinum (ref.7) was obvious : this is , however , a less satisfactory reaction because of the slower kinetics involved in d^6 platinum(IV) with respect to d^8 gold(III) , but the reaction is clean and only one single product is obtained , $PtCl_2(CO)_2$, for reasons that have been completely clarified and will become evident in the course of this paper . It is important to realize that these syntheses are examples of redox processes promoted by carbon monoxide, the oxidized product being $COCl_2$.

The use of thionyl chloride as a reaction medium allowed us to solve a debated problem existing in the literature (ref.9) about the existence of a chlorocarbonyl complex of palladium (II) . The dimeric $Pd_2Cl_4(CO)_2$ could be easily prepared (ref.2) by the reaction of $PdCl_2$ with CO at superatmospheric pressure of CO:

$$2 \ PdCl_{2(s)} \ + \ 2 \ CO_{(SOCl_2)} \ \rightleftharpoons \ Pd_2Cl_4(CO)_{2(SOCl_2)} \quad\quad (1)$$
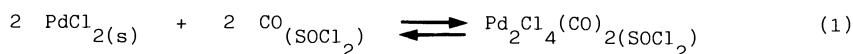
An important point is that reaction (1) , contrary to those mentioned above with gold(III) and platinum(IV) , does not involve a change of the oxidation state of the palladium substrate . As a matter of fact , no reduction of palladium(II) to lower oxidation states was ever observed under these conditions .
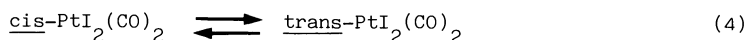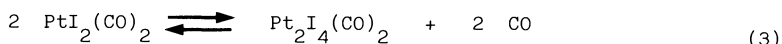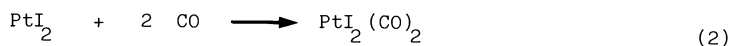
FURTHER SYNTHETIC WORK AND THE NATURE OF THE M—CO BOND

The detailed study (ref.10) of reaction (1) has established that the formation of $Pd_2Cl_4(CO)_2$ is exothermic ($\Delta H° = -13.6 \pm 0.2$ kcal per mol of dimer ; $\Delta S° = -30.8 \pm 0.8$ eu) . These results allowed us to estimate a value of about 24 kcal for the $Pd(II)-CO_t$ (CO_t = terminal CO) bond energy . This appears to be a reasonable value when considering that we are dealing with a 4d element , that the strength of transition metal-C bonds increases on descending a Group of metals and that the $Fe(II)-CO_t$ bond energies were estimated (ref.11) to be 15.3 kcal and 17.5 kcal for $FeBr_2(CO)_4$ and $FeI_2(CO)_4$, respectively . However , the unstable nature of the tetracarbonyls had still to be explained , especially considering that the heats of sublimation (ref.12) of the elements increases in the sequence Pd (91 kcal) , Ni (102.8 kcal) , Pt (135.2 kcal) , and $Ni(CO)_4$, of course is going to celebrate soon its centennial anniversary (ref.13) . Of course , the metals of the nickel subgroup are electronically bound not to exceed the number of four bonds to CO , being therefore in an unfavourable situation with respect to the other elements on their left in the Periodic Table . Moreover , an uniquely weak $M-CO_t$ bond was suggested for palladium(0) by the observation that it has the lowest sublimation energy in the triad .

Following these considerations a little further and having observed , together with other workers (ref.14) , that the complexes in this area of the Periodic Table are characterized by exceedingly high $\tilde{\nu}_{CO}$'s , the provisional suggestion was made that palladium and platinum could not form $M-CO_t$ bonds strong enough to compensate for the sublimation energy of the metals and for the entropy change involved in the formation of $M(CO)_4$. A further hypothesis was that no sufficient strengthening of the bond was necessarily obtained by decreasing the oxidation state of the metal , if , especially for palladium and perhaps silver , the M-CO bond was predominantly σ in nature . There are several ways to test this hypothesis . We reasoned that the M-CO bond would be sensitive to changes in the rest of the molecule , the halide ligand being the obvious choice for studying electronic effects trasmitted through the metal . An effort has therefore been made to synthesized new halo-carbonyl complexes of platinum(II) and palladium(II) , concentrating the attention on the iodo-complexes , which had not been prepared earlier or had been studied incompletely for reasons which become quite evident in the course of the investigation .

Malatesta and Naldini had pointed out earlier (ref.15) that the robustness of halo-carbonyl complexes of platinum(II) , of general formula $Pt_nX_{2n}(CO)_2$ (n=1,2) , decreases along the series $Cl > Br > I$. This is quite remarkable since for halo-carbonyl complexes of metals in the middle section of the transition series the sequence of robustness is believed to be the opposite.

It has now been possible to establish (ref.16) that PdI_2 suspended in a hydrocarbon or in a halogenated solvent is readily converted into $PtI_2(CO)_2$ at atmospheric pressure and room temperature :

$$PtI_2 \ + \ 2 \ CO \ \longrightarrow \ PtI_2(CO)_2 \quad\quad (2)$$

$$2 \ PtI_2(CO)_2 \ \rightleftharpoons \ Pt_2I_4(CO)_2 \ + \ 2 \ CO \quad\quad (3)$$

$$\underline{cis}\text{-}PtI_2(CO)_2 \ \rightleftharpoons \ \underline{trans}\text{-}PtI_2(CO)_2 \quad\quad (4)$$

The monomeric $PtI_2(CO)_2$ is characterized by one single CO stretching vibration , thus suggesting a $\underline{trans}$-structure for it . However , the spectra of the compound in different solvents show a second weak band (at 2147 cm^{-1} in toluene) which is believed to be due to a small amount of the $\underline{cis}$-isomer in equilibrium , see equation (4) , the second band of $\underline{cis}$-$PtI_2(CO)_2$ being not
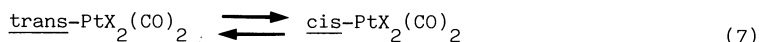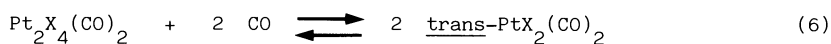
well resolved due to the intense absorption of the trans-isomer . The formation of the mono-
mer di-iodo di-carbonyl from PtI_2 is substantially complete at atmospheric pressure of CO ,
but equilibrium (3) is promptly established at reduced CO pressure and the dimer $Pt_2I_4(CO)_2$
is formed and can be easily separated thanks to its lower solubility . The dimeric compound
has been investigated (ref.16) by X-ray diffraction method and the compound has been shown to
consist of iodide-bridged $Pt_2I_4(CO)_2$ units , each platinum atom being surrounded in a square
geometry by two bridging iodides , one terminal iodide and the carbonyl group . The $Pt-I_b$
(I_b = bridging iodide) distance is only slightly longer (av.,2.626(3) Å) than the $Pt-I_t$ bond
distance of 2.596(3) Å , and the Pt...Pt nonbonding distance is 3.846(2) Å .

The three dimers $Pt_2X_4(CO)_2$ are thermodynamically unstable with respect to the corresponding
monomers at atmospheric pressure of CO , see equation (5) , indipendent of the halogen bonded
to platinum . The equilibrium constants are large in all three cases (the solubility of CO
(ref.17) in organic solvents is around $7 \cdot 10^{-3}$ M) , in spite of the fact that the reaction to
form the monomer should not be entropically favoured .

$$Pt_2X_4(CO)_2 \quad + \quad 2CO \quad \rightleftharpoons \quad 2 \quad PtX_2(CO)_2 \qquad (5)$$
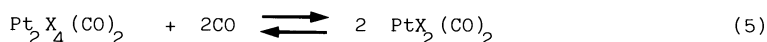
The formation of the monomer from the dimer involves stabilization arising from the loss of
two platinum bridging halide bonds ($Pt-X_b$) per platinum in the reagent and the formation of
one platinum-terminal X bond ($Pt-X_t$) and one Pt-CO bond . It has already been pointed out
that the differences in bond distances between $M-X_b$ and $M-X_t$ become progressively smaller a-
long the sequence Cl>Br>I in iridium(III) complexes (ref.18) , i.e. for a cation which does
not require the formation of the M-M bond . Thus , if for the bridged iodide complex of pla-
tinum(II) we make the reasonable assumption that the energy associated with $Pt-I_b$ is not lar-
gely different from that of the $Pt-I_t$ bond , we come to the immediate conclusion that Pt-I
should be similar in energy to $Pt-CO$. An estimate of the $Pd-Cl_t$ and $Pd-Cl_b$ bond energies
for $PdCl_2$ is 62 and 48 kcal , respectively , and platinum-halogen bonds are believed to be
stronger than palladium-halogen bonds (ref.20) .

The study of the reaction of the platinum(II) dimers with carbon monoxide , see equation (5),
led us to intercept the kinetically controlled intermediate trans isomer of $PtCl_2(CO)_2$ along
the sequence to the thermodynamically stable cis-$PtCl_2(CO)_2$. These observations have now
been extended to include the bromo and iodo derivatives . While $Pt_2Br_4(CO)_2$ behaves in a simi-
lar manner to $Pt_2Cl_4(CO)_2$, the iodo complex does not follow the same pattern . More specifi-
cally , while the trans monomeric species of the chloro and bromo derivatives are thermodyna-
mically unstable compounds and become observable only by virtue of a modest kinetic barrier
to their isomerization , trans-$PtI_2(CO)_2$ is the predominant species in solution and we could
detect only small concentrations of the cis isomer in equilibrium with it . Thus equilibrium
(7) is almost completely shifted to the left in the case of X=I . We believe that this observation
alone does not lend itself to much speculation about the nature of the Pt-CO bond , since
steric effects could be sufficient to explain the observed geometry . We could , however , an-
ticipate that overwhelming π-back bonding effects should not be operating in $PtI_2(CO)_2$ becau-
se they should favour the cis-isomer .

$$Pt_2X_4(CO)_2 \quad + \quad 2 \quad CO \quad \rightleftharpoons \quad 2 \quad \text{trans-}PtX_2(CO)_2 \qquad (6)$$

$$\text{trans-}PtX_2(CO)_2 \quad \rightleftharpoons \quad \text{cis-}PtX_2(CO)_2 \qquad (7)$$

We have verified the possibility of obtaining the bromo and iodo carbonyl derivatives of pla-
tinum(II) by halogen exchange reactions in hydrocarbon solution with dry HX , X=Br , I , see
equation (8) . Beside giving us the possibility of obtaining the compounds without the preli-

$$PtCl_2(CO)_2 \quad + \quad 2\,HX \quad \xrightarrow{\text{toluene}} \quad PtX_2(CO)_2 \quad + \quad 2 \quad HCl \qquad (8)$$
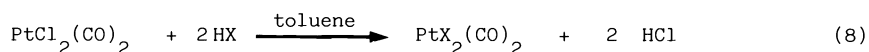
minary requirement of preparing the starting PtX_2 , reaction (8) lends itself to some intere-
sting considerations about the nature of the Pt-X bond . We believed that the observed exchan-
ge is driven by the formation of HCl , the ΔG_f° for HCl , HBr and HI (ref.21) being -22.77 ,
-12.73 and +0.38 kcal/mol , respectively . This amounts to saying that the observed exchange
reaction (8) cannot be taken as an evidence of a decreased stability of the halo-carbonyl
complexes of platinum(II) in the sequence I>Br>Cl .

Relevant to the discussion of the relative stabilities of halo-carbonyl complexes of platinum (II) and palladium(II) (for the latter compounds the available data are still limited) , are the i.r. CO stretching vibrations and the ^{13}C NMR spectra (ref.16) . Our data are often complementary to those obtained earlier by other workers . With the inclusion of the iodides for the neutral species which are frequently missing , and of the trans-$PtX_2(CO)_2$ complexes which have now become available , the trend to a decrease of ν_{CO}'s in the sequence Cl>Br>I is completely confirmed . Typical CO stretching vibrations are for example : cis-$PtX_2(CO)_2$, toluene , 2170 (Cl) , 2162 (Br) , 2147 (I) cm^{-1} , only the high wavenumber band reported ; Pt_2X_4-$(CO)_2$, heptane , 2130 , 2122 , 2106 cm^{-1} . As for the ^{13}C NMR spectra , our data confirm those published earlier (ref.14) , namely that the J_{Pt-C} decrease in the sequence Cl>Br>I . According to the accepted theoretical treatment (ref.22) , the largest contribution to the J_{Pt-C} coupling constant comes from the Fermi contact term , which is related , inter alia , to the s character of the hybrids used by the atoms in the bond and to the electron densities of 6s(Pt) and 2s(C) orbitals at the corrisponding nuclei .
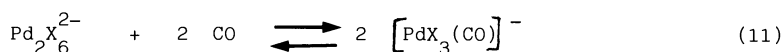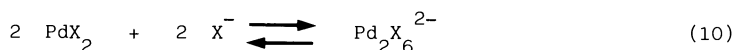
Our results on halo-carbonyl complexes of platinum(II) are similar to those reported earlier (ref.23) for the J_{Pt-P} in halo-tertiary phosphine complexes of platinum(II) by Venanzi and co-workers . Beside decreasing within each series from chloride to iodide , the J_{Pt-C} for the halo-carbonyl complexes decrease in the sequence : $Pt_2X_4(CO)_2 > [PtX_3(CO)]^- >$ cis-$PtX_2(CO)_2 >$ trans-$PtX_2(CO)_2 > [PtX_5(CO)]^-$. In agreement with literature data (ref.24) on several systems containing NMR-active X-Y bonds for which the corrisponding J_{X-Y} could be measured , we shall assume that larger J_{Pt-C} values are associated with stronger Pt-C σ bonds and that , therefore , the strength of the Pt-CO σ bond decreases in these complexes along the Cl>Br>I sequence . A further point of interest for the ^{13}C NMR data is that the J_{Pt-C} for the cis and trans series of $PtX_2(CO)_2$ are only slightly different (e.g. in $SOCl_2/CD_2Cl_2$ cis-$PtCl_2(CO)_2$ and trans-$PtCl_2(CO)_2$ have J_{Pt-C} of 1586.2 and 1564.6 Hz , respectively) . In other words , it appears that the Pt-C σ bond is about the same in both geometrical isomers . Consistent with this , is the observation already mentioned earlier that cis and trans-$PtI_2(CO)_2$ are in equilibrium . Interesting and quite important for the discussion concerning the nature of the Pt-CO bond in these systems , is the observation that the smallest J_{Pt-C} was observed for the platinum(IV) carbonyl derivatives $[PtX_5(CO)]^-$, in agreement with the fact that two more orbitals (d and p) have to be used by the central metal atom on going from the square coordination of platinum(II) to the pseudo-octahedral of platinum(IV) . Furthermore and more importantly , the J_{Pt-C} decreases from Cl to Br in $[PtX_5(CO)]^-$ as it does in platinum(II) series . Thus , a mechanism other than π-back bonding , which is out of question in platinum(IV) derivatives and based on predominantly σ-contributions , should be capable of explaining the change of J_{Pt-C} with the halogen .

The dimeric carbonyl of palladium(II) , $Pd_2Cl_4(CO)_2$,was reported earlier . The corresponding unstable bromo derivative has now been isolated (ref.16) , although always contaminated by some $PdBr_2$, the latter arising from the cleavage of the Pd-CO bond , equilibrium (9) being shifted to the left at atmospheric pressure , much more for the bromo than for the chloro derivative (ref.2) . The bromo-carbonyl was obtained from $PdBr_{2(s)}$ and CO at superatmospheric

$$2 \; PdX_{2(s)} \; + \; 2 \; CO_{(solv)} \rightleftarrows Pd_2X_4(CO)_{2(solv)} \qquad (9)$$
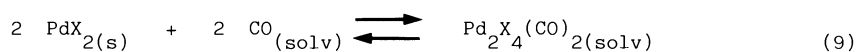
pressure and then by quencing the resulting solution at dry-ice temperature . The trans-dimeric structure similar to that suggested for $Pd_2Cl_4(CO)_2$ and now established for $Pt_2I_4(CO)_2$ is probable on the basis of the single CO stretching vibration observed at 2148 cm^{-1} in toluene, to be compared with 2162 cm^{-1} in the same solvent for $Pd_2Cl_4(CO)_2$. Attempts to carbonylate PdI_2 at superatmospheric pressure of CO or to prepare $Pd_2I_4(CO)_2$ by halogen exchange from $Pd_2Cl_4(CO)_2$ failed and the latter reaction led to PdI_2 , thus confirming that the exchange had occurred ($PdCl_2$ does not exchange with $HI_{(g)}$ under comparable conditions) but the platinum-carbonyl iodide formed would promptly decarbonylate according to equilibrium (9).

It has , however , been possible to prepare $[PdI_3(CO)]^-$ by reaction of PdI_2 with CO in the presence of I^- (NBu_4I was the carrier of iodide in sym-dichloroethane solution) , see equation (10) . However , in agreement with the trend already established for all these systems , the iodo anionic compound was unstable and CO dissociation was observed even in the solid state at room temperature .

$$2 \ PdX_2 \ + \ 2 \ X^- \ \rightleftharpoons \ Pd_2X_6^{2-} \qquad\qquad (10)$$

$$Pd_2X_6^{2-} \ + \ 2 \ CO \ \rightleftharpoons \ 2 \ \left[PdX_3(CO)\right]^- \qquad\qquad (11)$$

CONCLUSIONS

The new data obtained for the series of platinum(II) carbonyl complexes $Pt_2X_4(CO)_2$, cis-Pt-$X_2(CO)_2$, trans-$PtX_2(CO)_2$, with the inclusion of the iodo derivatives and the isolation of $Pd_2Br_4(CO)_2$, the i.r. data and the ^{13}C NMR spectra , together with the established chemistry appear to allow us to draw the conclusion that the stability of platinum(II) and palladium (II) carbonyl complexes decreases along the sequence Cl>Br>I . The iodo complexes were always the least stable ones for both platinum(II) and palladium(II) and no evidence for the forma-tion of $Pd_2I_4(CO)_2$ could be gathered , whereas $Pd_2Br_4(CO)_2$ was shown to revert to $PdBr_2$ at atmospheric pressure of CO , to be compared with the earlier data for the $PdCl_2$/CO system. The observed trend of stabilities could be due , of course , to a weaker M—CO bond in the a-bove mentioned halide sequence , or to a weaker M—X bond in the same sequence , or both . We prefer the third explaination , i.e. that both M—CO_t and M—X bonds tend to become weaker a-lonf the Cl>Br>I sequence , although no firmly established quantitative data are available as yet to confirm this hypothesis . The J_{Pt-C} coupling constants suggest a decreased σ contribu-tion to the Pt—CO bond along the series Cl>Br>I of halide ligands . The fact that J_{Pt-C} de-crease from the lighter to the heavier halide both for the platinum(II) complexes and for the platinum(IV) derivatives $\left[PtX_5(CO)\right]^-$,X=Cl , Br , suggests that π-bonding is not an exclusive requirement to explain the observed facts . If in fact the σ component to the Pt—CO_t bond is predominant , the increase of $\tilde{\nu}_{CO}$'s in the sequence I<Br<Cl may be due to a progressively larger transfer of electron density from the 5σ orbital of CO , with a slight antibonding character (ref.25) . Removal of one electron from this orbital (ref.26) to produce CO^+ would reduce the CO distance from 1.128 to 1.115 $\overset{\circ}{A}$, while the $\tilde{\nu}_{CO}$ increases slightly from 2143 cm^{-1} to 2184 cm^{-1} .

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