Journal of Organometallic Chemistry, 354 (1988) 357–368
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Carbonyl complexes of noble metals with halide ligands

I. Platinum(II)/halide exchange, dimerization, isomerization, ^{13}C NMR data and crystal and molecular structure of $Pt_2I_4(CO)_2$

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(Received January 4th, 1987)

Abstract

Room temperature and atmospheric pressure carbonylation of PtI_2 in toluene gave *trans*-$PtI_2(CO)_2$ as the predominant isomer, together with *cis*-$PtI_2(CO)_2$. Lowering of p(CO) resulted in conversion of $PtI_2(CO)_2$ into $Pt_2I_4(CO)_2$ both in solution and in the solid state. The iodide-bridged centrosymmetric $Pt_2I_4(CO)_2$ was studied by single crystal X-ray diffractometry. Monoclinic; space group $C2/c$; a 10.772(2); b 9.077(1); c 13.001(3) Å; β 112.26(2)°; U 1176.5(5) Å^3; $Z = 4$; D_{calc} 5.385 g cm^{-3}; Mo-K_α radiation (λ 0.71069 Å); μ(Mo-K_α) 343.6 cm^{-1}; $F(000) = 1584$. The structure consists of $Pt_2I_2(\mu\text{-}I)_2(CO)_2$ units with tetracoordinated square planar platinum bonded to two bridging iodides, one terminal iodide and one terminal CO group. The Pt...Pt nonbonding distance is 3.846(2) Å. A new preparative procedure for the monomeric halo carbonyls $PtX_2(CO)_2$ (X = Br, I) involves treatment of *cis*-$PtCl_2(CO)_2$ with dry HX in toluene. Addition of CO to $Pt_2Br_4(CO)_2$ occurs readily to give *cis*-$PtBr_2(CO)_2$ through the transient *trans*-$PtBr_2(CO)_2$. The ^{13}C NMR spectra data for the platinum complexes show that: (a) values of J(Pt–C) decreases in the sequence $Pt_2X_4(CO)_2 > [PtX_3(CO)]^- >$ *cis*-

$PtX_2(CO)_2 \gtrsim$ *trans*-$PtX_2(CO)_2 > [PtX_5(CO)]^-$; (b), within each series of compounds, values of J(Pt–C) decrease in the sequence Cl > Br > I.

Introduction

The contrast between the non-existence of the carbonyls $Pd(CO)_4$ and $Pt(CO)_4$ as stable isolable species and the long-known existence of $Ni(CO)_4$ has provided one of the conceptual puzzles of metal carbonyl chemistry [1a]. A recent theoretical treatment [1b] was concerned with comparison of the M–CO intrinsic mean bond energies for the tetracarbonyl species $M(CO)_4$ (M = Ni, Pd, Pt). In the course of our investigation on palladium(II) carbonyl derivatives, we have shown that the formation of $Pd_2Cl_4(CO)_2$ from $PdCl_{2(s)}$ and CO in thionyl chloride is an exothermic reaction [2]. The Pd^{II}–CO_t (CO_t = terminal carbonyl) bond energy is estimated to be ca. 24 kcal, and it has been suggested that the intrinsically poor π-back bonding contribution in the Pt–CO_t and Pd–CO_t systems can account for the instability of the zerovalent compounds, there being no substantial increase in bond energy upon lowering the oxidation state of the metal. That the Pd–CO and Pt–CO bonds should be predominantly σ-type is also suggested by the high reactivity of these compounds towards nucleophiles such as amines and water [3]. If the σ-component of the M–CO_t bond is dominant, a study of the effect of the halide on the properties of halocarbonyl complexes appeared to provide a prospect of gaining further insight into this problem.

Malatesta and Naldini [4] some years ago pointed out that the thermal stability of halocarbonyl complexes of platinum(II) in the sequence Cl > Br > I decreases. This is remarkable, since for halocarbonyl complexes of many typical transition metals (e.g., chromium(0), tungsten (0), manganese(I), rhenium(I)), the sequence of thermal stability is believed to be the opposite, i.e. Cl < Br < I. Connor pointed out [5] that the calorimetric dissociation energy for Fe–CO is about 15 kcal in $FeBr_2(CO)_4$ and 17 kcal in $FeI_2(CO)_4$.

The monomeric halocarbonyl complexes of platinum(II) of formula $PtX_2(CO)_2$ were reported earlier (X = Cl [6], Br [4], I [4]), but there remained some doubt about the iodo derivative, which had not been studied to any considerable extent after the pioneering work by Malatesta and Naldini, who obtained it by treating PtI_2 with CO at high pressure and temperature.

We present here some new information on bromo and iodo derivatives of platinum(II), clarify the behaviour of the PtI_2/CO system in solution and report the crystal and molecular structure of $Pt_2I_4(CO)_2$ along with some new ^{13}C NMR data. These data, combined with those presented in Part II, (following paper) give new information about the effect of the halide ligand on the properties of these systems.

Experimental

The IR spectra were recorded on a Perkin–Elmer model 283 instrument equipped with grating: each spectrum was calibrated with both CO and water vapour, and the wavenumbers are believed to be accurate to within ± 1 cm^{-1}. The ^{13}C NMR spectra were recorded at 50.28 MHz with a Bruker WP 200 spectrometer, under the following conditions: sweep width, 15000; flip angle, 12 μsec (ca. 50°); relaxation delay, 3 sec; {^{1}H} decoupler off; size, 16k points; number of scans, 4k–20k. Chemical shifts (Table 4) are in ppm from tetramethylsilane. Since the spectra were run without decoupling, no differences in the NOE have to be considered. Whenever possible we confirmed that integration ratios between the central peak due to the Pt isotope ($I = 0$) and the satellites due to the ^{195}Pt isotope ($I = \frac{1}{2}$) corresponded to the isotopic abundances. The rather long relaxation delay used and the low flip angle ensured complete relaxation between pulses and allowed quantitative analysis when necessary.

Unless otherwise stated, all the operations were carried under dinitrogen. Solvents were dried by conventional methods prior to use. The iodide PtI_2, prepared by a known procedure [7], was found to have a lower Pt content (39.8%) than expected (43.5%) after being dried in vacuo at room temperature, indicating the presence of some unknown impurities. The yields of carbonylation throughout this paper are based on the platinum content of the starting iodide. The compound [8] *cis*-$PtCl_2(CO)_2$ was prepared by a reported method [8]. The dimer $Pt_2Cl_4(CO)_2$ was prepared as previously described [9], with an important modification which involves the addition of $SOCl_2$ to the solution of $[PtCl_3(CO)]^-$ in concentrated hydrochloric acid. Such a solution was obtained by adding 3.746 g (11.63 mmol) of *cis*-$PtCl_2(CO)_2$ to 25 cm^3 of concentrated aqueous HCl and stirring vigorously for about 8 h at room temperature. To the resulting golden yellow solution, 170 cm^3 of $SOCl_2$ were rapidly added from a dropping funnel, during which gas (SO_2 + HCl) was evolved and the temperature of the reaction mixture spontaneously remained below 0 °C owing to the endothermic nature of the reaction. The addition of $SOCl_2$ was completed in about 30 min. The solution was filtered to remove small amounts of a solid product and the filtrate was concentrated to about half its volume, treated with 100 cm^3 of heptane, then kept at ca. −80 °C. The dimer that separated was filtered off and dried in vacuo (2.15 g, 63% yield).

The dibromo derivative *cis*-$PtBr_2(CO)_2$ was prepared previously either by carbonylation [4] of $PtBr_6^{2-}$ under a high pressure of CO at high temperature, or by treatment [10] of $PtBr_2$ with CO at 220 °C. We have made it by a new procedure in which the dichloro derivative *cis*-$PtCl_2(CO)_2$ (1.174 g, 3.65 mmol) was dissolved in 20 cm^3 of toluene and treated with dry HBr at room temperature. The operation was repeated three times, and IR monitoring of the reaction showed that appearance of new bands at 2162 and 2740 cm^{-1}, due to *cis*-$PtBr_2(CO)_2$ and dissolved HCl, respectively (HBr present absorbs at 2440 cm^{-1}). The resulting solution was concentrated to about half its volume under reduced pressure, heptane (20 cm^3) was added, and the solution kept at ca. 0 °C to assist crystallization. The colourless crystals of *cis*-$PtBr_2(CO)_2$ were collected by filtration and dried in vacuo (65.6% yield). The compound reacted rapidly with PPh_3 with quantitative evolution of CO. Found: CO, 13.6. $C_2Br_2O_2Pt$ calcd.: CO, 13.6%. In a control experiment carried out involving use of a stoicheiometric amount of HBr, it was established that the chloride displacement was complete in ca. 10 min.

Preparation of $PtI_2(CO)_2$

(A) From PtI_2 and CO at atmospheric pressure. Platinum(II) iodide corresponding to 5.90 mmol of platinum was suspended in toluene (50 cm^3) and treated with CO at atmospheric pressure. After about 1 h the solid had almost completely disappeared: the mixture was stirred for 12 h and a clear orange solution was

obtained. This was kept at dry-ice temperature so that the iodo derivative crystallized out, it was collected on a filter maintained at low temperature and then dried under reduced pressure at low temperature under a stream of carbon monoxide and then sealed in vials under CO (55% yield). In spite of all precautions taken, the monomeric $PtI_2(CO)_2$ so obtained rapidly underwent conversion into the dimer $Pt_2I_4(CO)_2$ at room temperature, even in the solid state, if the partial pressure of CO was reduced below 1 atm. The compound was analyzed for its CO content by reaction with a fourfold molar excess of PPh_3 at 24.9 °C in a gas-volumetric apparatus. Found: CO, 10.8. $C_2I_2O_2Pt$ calcd.: Pt: CO, 11.1%. In a control gas-volumetric experiment, PtI_2 corresponding to 0.74 mmol of platinum was suspended in toluene (20 cm^3) and treated with CO at atmospheric pressure at 24.9 °C. After about 1 h stirring, the amount of CO absorbed corresponded to 94.6% of the expected amount for formation of $PtI_2(CO)_2$. For details of the analytical data for $PtI_2(CO)_2$, see the subsequent section on $Pt_2I_4(CO)_2$.

(B) From cis-$PtCl_2(CO)_2$ and HI. The dichloro derivative (1.102 g, 3.42 mmol) was dissolved in toluene (20 cm^3) the flask was evacuated, and dry HI was slowly introduced at room temperature. After 2 h the IR spectrum of the solution showed the presence of three platinum carbonyl species, namely *cis*-$PtCl_2(CO)_2$ (2170 cm^{-1} *), *cis*-$PtI_2(CO)_2$ in small concentration (2147 and about 2110sh cm^{-1}), and *trans*-$PtI_2(CO)_2$ (2121 cm^{-1}). The treatment with HI was repeated twice and after 4 h only the iodo complexes were present. The flask was then filled with CO at atmospheric pressure and the contents stirred at room temperature for a further 2 h. The solution was kept at about −80 °C, and the iodocarbonyl $PtI_2(CO)_2$ that separated was isolated by filtration as described under A), 41.7% yield.

Thermal behaviour of $PtX_2(CO)_2$. (A) X = Cl. The dichloro derivative (0.561 g, 1.74 mmol) was dissolved in thionyl chloride (20 cm^3, b.p. 78.8 °C) under dinitrogen and the solution was refluxed for 3.5 h. Monitoring by IR showed that the starting material remained unchanged, and no solid products were formed.

(B) X = Br. The bromo derivative *cis*-$PtBr_2(CO)_2$ (0.945 g, 2.30 mmol) was dissolved under dinitrogen in n-hexane (20 cm^3, b.p. 69 °C) and the solution was refluxed for 20 min than cooled to room temperature. The IR spectrum of the supernatant solution showed bands in the carbonyl stretching region due to unchanged starting materials. After 13 h reflux no starting material remained. The mixture was cooled to room temperature and the orange $Pt_2Br_4(CO)_2$ was filtered off and dried in vacuo (57% yield).

(C) X = I. A sample of the monomeric $PtI_2(CO)_2$ was introduced into a Schlenk tube, which was connected to a vacuum pump and maintained at room temperature. After some minutes, the solid became red violet. The IR spectrum of the solution, obtained by partial dissolution of the solid in n-heptane showed only bands due to $Pt_2I_4(CO)_2$ (see next section).

Preparation of $Pt_2I_4(CO)_2$. A sample of PtI_2 (2.33 g) corresponding to 5.18 mmol of platinum was suspended in 100 cm^3 of toluene under carbon monoxide at room temperature (about 20 °C). After 12 h stirring, the suspension was filtered to eliminate a small amount of a dark residue. The solution, which contained $PtI_2(CO)_2$,

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* The band at 2126 cm^{-1} was overlapped with that of *trans*-$PtI_2(CO)_2$.

as shown by the IR spectrum, was evaporated to dryness under reduced pressure. A suspension of dark violet residue in n-pentane (150 cm^3) was stirred for 12 h under carbon monoxide at 24 °C in a thermostated bath and the violet dimer $Pt_2I_4(CO)_2$ formed was filtered off, briefly dried in vacuo (0.5 h), and sealed in vials under dinitrogen (1.7 g, 68.8% yield). The CO content of the dimer was determined in the following manner. The substance (0.4136 g, 0.433 mmol) was sealed in a thin-walled flask and introduced into a gas-volumetric apparatus together with toluene (20 cm^3) pre-saturated with CO. When thermal equilibrium had been reached (at 26.5 °C), the flask containing the sample of the dimer was broken mechanically and the absorption of CO (0.823 mmol) give the monomer $PtI_2(CO)_2$ was complete in about 1 h. A solution of PPh_3 was then added and the CO evolved in the formation of $PtI_2(PPh_3)_2$ corresponded to 1.64 mmol. By subtracting the amount of CO absorbed for the formation of the monomer in the first part of the experiment, the CO content of the dimer was calculated to be 5.5% ($C_2I_4O_2Pt_2$ calcd.: CO, 5.9%).

X-Ray data collection and reduction of $Pt_2I_4(CO)_2$. Crystals suitable for the X-ray study were grown from a saturated toluene solution. A crystal of approximate dimensions (mm) 0.23 × 0.31 × 0.37 sealed in a glass capillary was mounted on a Philips PW 1100 single-crystal diffractometer (graphite-monochromated Mo-K_α radiation). The unit cell dimensions and their standard deviations were obtained by a least-squares fit to the ϑ values of 20 well-centred reflections chosen from a variety of points in reciprocal space. Crystal data: $M = 953.8$; monoclinic,; space group $C2/c$; a 10.772(2); b 9.077(1); d 13.001(3) Å; β 112.26(2)°; U 1176.5(5) $Å^3$; $Z = 4$; $D_c = 5.385$ g cm^{-3}; Mo-K_α radiation (λ 0.71069 Å); μ(Mo-K_α) 343.6 cm^{-1}; $F(000) = 1584$. Examination of the systematic absences (hkl, $h + k = 2n + 1$ and $h0l$, $h = 2n + l$, $l = 2n + 1$) identified the space group as $C2/c$ or Cc. The choice of the former was based on the E value statistics, which showed the crystal to be centrosymmetric. Intensity data were recorded at room temperature up to 2ϑ 50.0 °, using an ω scan, a scan rate of 0.075° s^{-1} and a scan width of 1.6°. The reflections in the quadrant $\pm h + k + l$ were collected, except for those with $h + k$ odd. A total of 1158 reflections were obtained, of which 1041 were unique ($R_{int} = 0.0788$). After correction for Lorentz and polarization factors as well as for absorption and extinction effects, the 748 reflections having $I > 3\sigma(I)$ were merged to leave 718 unique reflections, which were used in subsequent calculations. The absorption correction was accomplished by a semiempirical method based on ψ scans (0–180 °, every 10 °) of two reflections with χ value near 90 °. One standard reflection recorded every hour, showed no significant variation. The structure was solved by the heavy-atom technique. The Pt and I atom were located from a Patterson map. After a partial isotropic refinement of their positional parameters by a least-squares procedure, the oxygen and carbon coordinates were obtained from a difference Fourier map phased on the contribution of the heavy atoms. Satisfactory refinement of anisotropic thermal parameters was possible for platinum and iodine only, and extension of such refinement to oxygen and carbon resulted in convergence difficulties and so their thermal parameters were kept isotropic. Omitted in the last cycle of refinement were 25 reflections with intensities at the limit of observation and 15 reflections with bad agreement between F_o and F_c. The final residual indices for 36 variables refined for 678 reflections were $R = 0.0589$, $R_w = 0.0815$, GOF = 0.8220, with weights $w = [\sigma^2(F_o) + 0.00719\ F_o^2]^{-1}$. The final difference map revealed two relevant residual peaks of about 3.7 e $Å^{-3}$ in the vicinity of the platinum atom.

Table 1

Fractional atom coordinates ($\times 10^4$) with estimated standard deviations in parentheses for $Pt_2I_4(CO)_2$

Atom	x/a	y/b	z/c
Pt	1740(1)	−849(1)	784(1)
I(1)	−696(2)	−1185(2)	742(2)
I(2)	2611(3)	−2941(3)	2244(2)
O	4507(27)	−467(30)	920(25)
C	3517(24)	−632(26)	887(23)

Complex atom scattering factors were employed and the heavy atoms were corrected for anomalous dispersion effects, both real and imaginary [11]. Computing was carried out with the SHELX76 crystallographic programme [12] on the CDC Cyber 76 computer of CINECA, Casalecchio, Bologna. The molecular plots were drawn by ORTEP [13] and PLUTO [14]. The final atomic coordinates are shown in Table 1.

Reactions of $Pt_2X_4(CO)_2$ with CO (A) $X = Br$. The dimer $Pt_2Br_4(CO)_2$ (0.089 g, 0.116 mmol) was dissolved in *sym*-$C_2H_2Cl_4$ under an atmosphere of dinitrogen. The IR spectrum showed the carbonyl stretching vibration of the dimer at 2127 cm^{-1}. Carbon monoxide at atmospheric pressure was then introduced at 0 °C. The IR spectrum of the solution recorded 3 min later showed a new band at 2142 cm^{-1} attributed to *trans*-$PtBr_2(CO)_2$. Carbon monoxide was pumped off and replaced by dinitrogen and the IR spectrum recorded after several hours stirring showed complete conversion into the *cis*-isomer ($\tilde{\nu}$(CO) 2170, 2130 cm^{-1}). In another experiment, 0.499 g (0.652 mmol) of the dimer were dissolved in 15 cm^3 of *sym*-$C_2H_2Cl_4$ and treated with CO at atmospheric pressure at 0 °C. After about 3 min, dinitrogen was introduced into the flask and heptane (30 cm^3) was added to the solution cooled to dry-ice temperature. The solid *trans*-$PtBr_2(CO)_2$ was collected on a pre-cooled filter, washed with pentane, and dried briefly in vacuo (35.2% yield). The solid, which had been kept in sealed vials at about −30 °C, was converted into the *cis*-isomer within one day.

(B) $X = I$. A sample of the dimer $Pt_2I_4(CO)_2$ (0.733 g, 0.768 mmol) was dissolved in benzene (17.358 g) at room temperature under dinitrogen. The IR spectrum showed the carbonyl stretching band of the dimer at 2104 cm^{-1}. When CO was introduced, $PtI_2(CO)_2$ was formed, as indicated by the appearance of the band of the *trans*-isomer at 2122 cm^{-1}, accompanied by a less intense band at 2148 cm^{-1} arising from a small amount of the *cis*-isomer. A cryoscopic determination gave a freezing point depression of 0.50° (found: 0.098 *m*; calcd.: 0.089 *m*) as further evidence of the transformation of the dimer into the corresponding monomer.

Results and discussion

Platinum(II) complexes. synthesis and reactivity

The bromo and iodo derivatives of platinum(II) can be obtained by a halogen exchange reaction in a hydrocarbon solvent (eq. 1). A similar exchange in aqueous medium was reported by Mylius and Foerster [15], who prepared $Pt_2Br_4(CO)_2$ from

$PtCl_2(CO)_2$ in concentrated hydrobromic acid, presumably through the intermediacy of $[PtBr_3(CO)]^-$. When $PtCl_2(CO)_2$ was treated with a stoichiometric

$$PtCl_2(CO)_2 + 2\ HX \xrightarrow[(X = Br,\ I)]{} PtX_2(CO)_2 + 2\ HCl \qquad (1)$$

amount of HBr, the exchange was complete at room temperature, the products, $PtBr_2(CO)_2$, HCl, and the reagent HBr giving rise to well separated IR absorptions. We believe that the driving force for the exchange reaction comes from the formation of HCl, the ΔG_f^0's for HCl, HBr, and HI being -22.77, -12.73 and $+0.38$ kcal/mol, respectively [16]. The exchange reaction (eq. 1) provides the best method currently available for the preparation of $PtBr_2(CO)_2$.

Although $PtI_2(CO)_2$ can also be prepared by reaction 1 from $PtCl_2(CO)_2$, it is better made by direct carbonylation of PtI_2. It has been shown that PtI_2 is readily converted to $PtI_2(CO)_2$ at atmospheric pressure at room temperature. The yields of carbonylation are substantially quantitative, see eqn. 2. Thus, a monomeric hydrocarbon-soluble halocarbonyl derivative of platinum(II) is now made available under mild conditions. This is a considerable improvement over earlier synthetic procedures equipment and elevated temperatures. This, combined with the fact that PtI_2 is readily available from aqueous $PtCl_4{}^{2-}$, makes $PtI_2(CO)_2$ an attractive new intermediate for reactions involving platinum(II).

The monomeric iodocarbonyl is characterized by a CO stretching vibration at 2120–2125 cm^{-1} (the exact position depending on the solvent), as shown in Table 2, and this suggests a *trans* structure. However, a second CO stretching band is observed at 2147 cm^{-1} in toluene, and this is attributed to small amounts of the *cis*-isomer, see eq. 3 *. This was confirmed by ^{13}C NMR measurements, as discussed later.

$$PtI_2 + 2\ CO \rightarrow PtI_2(CO)_2 \qquad (2)$$

$$cis\text{-}PtX_2(CO)_2 \rightleftharpoons trans\text{-}PtX_2(CO)_2 \qquad (3)$$

The three halocarbonyl complexes of platinum(II) undergo the reversible isomerization (eq. 3). For X = Cl and Br, the *cis*-isomer is the only observable species under equilibrium conditions, while for X = I the *trans*-isomer is considerably more stable, less than 5% of the *cis*-isomer being present.

In order to understand the chemistry of these systems fully, equilibrium 4 between the monomer and the dimer, governed by the CO partial pressure, must also be taken into account. Equilibrium 4 has been studied from both the monomer and the dimer sides. The monomeric chloro derivative is stable at the reflux

$$2PtX_2(CO)_2 \rightleftharpoons Pt_2C_4(CO)_2 + 2CO \qquad (4)$$

temperature of thionyl chloride and is converted into the corresponding dimer in refluxing benzene [4] and, more slowly, in refluxing hexane, whereas the bromo derivative dimerizes at the reflux temperature of hexane. On the other hand,

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* That we were dealing with a true equilibrium mixture of the two geometrical isomers was shown by the observation that solutions with similar spectroscopic properties were obtained irrespective of the method of preparation of $PtI_2(CO)_2$ (see Experimental section) and even after heating under CO (to avoid formation of the dimer).

Table 2

IR carbonyl stretching vibrations for halocarbonyl complexes of platinum(II)

Compound	$\tilde{\nu}$(CO) (cm^{-1})			
	n-heptane	toluene	dichloromethane [a]	*sym*-$C_2H_2Cl_4$ [a]
cis-$PtCl_2(CO)_2$ [b]	2167 2120	2170 2126		2179 2136
cis-$PtBr_2(CO)_2$ [c]	2156 2115	2162 2119		2170 2130
cis-$PtI_2(CO)_2$	2143 [d]	2147 [d]		2151 [d]
trans-$PtCl_2(CO)_2$				2150 [e]
trans-$PtBr_2(CO)_2$	2136	2136		2142
trans-$PtI_2(CO)_2$	2122	2121		2126
$Pt_2Cl_4(CO)_2$	2130	2128		2136
$Pt_2Br_4(CO)_2$	2122	2119		2127
$Pt_2I_4(CO)_2$	2106	2104		2110
$[PtCl_3(CO)]^-$ [f]			2098	
$[PtBr_3(CO)]^-$ [g]			2089	
$[PtI_3(CO)]^-$ [g]			2078	

[a] No halide exchange was observed in *sym*-tetrachloroethane or dichloromethane solutions of the bromo and iodo derivatives. [b] Bands at 2178 and 2137 cm^{-1} have been reported [10] for *cis*-$PtCl_2(CO)_2$ in benzene. [c] Bands at 2164 and 2122 cm^{-1} have been reported [10] for *cis*-$PtBr_2(CO)_2$ in benzene. [d] A band at about 2110 cm^{-1} is partly hidden by the absorptions due to *trans*-$PtI_2(CO)_2$. [e] Measured in thionyl chloride. [f] Tetra-n-propylammonium derivatives. [g] Tetra-n-butylammonium derivatives.

$PtI_2(CO)_2$ is completely converted into the dimer $Pt_2I_4(CO)_2$ at room temperature under a reduced pressure of CO.

The three $Pt_2X_4(CO)_2$ dimers are rapidly converted into the corresponding monomers under an atmospheric pressure of CO, in spite of the fact that the reaction should not be entropically favoured. We had previously studied [1a] the reaction of $Pt_2Cl_4(CO)_2$ with CO and intercepted the intermediate *trans*-$PtCl_2(CO)_2$ along the sequence leading to the *cis*-isomer. These observations have now been extended to the bromo and iodo derivatives. The complex $Pt_2Br_4(CO)_2$ behaves like $Pt_2Cl_4(CO)_2$, and the unstable *trans*-$PtBr_2(CO)_2$ could be isolated by carrying out the carbonylation of the dimer at low temperature, but the iodo complex behaves differently. The *trans* complexes $PtX_2(CO)_2$ (X = Cl, Br) are in fact, thermodynamically unstable, and are only observable by virtue of a small kinetic barrier to their isomerization. On the other hand, as mentioned above, *trans*-$PtI_2(CO)_2$ is the predominant species in solution, presumably due to the bulk of the iodide ligand [17*].

The new information acquired about equilibria 3 and 4 for the platinum iodide/CO system has been used in optimization of a new preparative procedure for $Pt_2I_4(CO)_2$. This compound can be prepared by direct carbonylation of PtI_2 in a two-step reaction **, involving the carbonylation to $PtI_2(CO)_2$ in toluene as solvent, followed by evaporation of the solvent and its substitution with n-pentane. In the light of equilibrium 4 for X = I, the use of a solvent with a relatively high vapour pressure is the best choice for maximizing the yield of the dimer under the

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* A reference number with an asterisk indicates a note in the list of references.

** We found it difficult to prepare pure PtI_2. Our method of preparing $Pt_2I_4(CO)_2$ does not require the use of pure PtI_2 since the first carbonylation in toluene to give the soluble $PtI_2(CO)_2$ followed by filtration removes the by-products originally present in PtI_2.

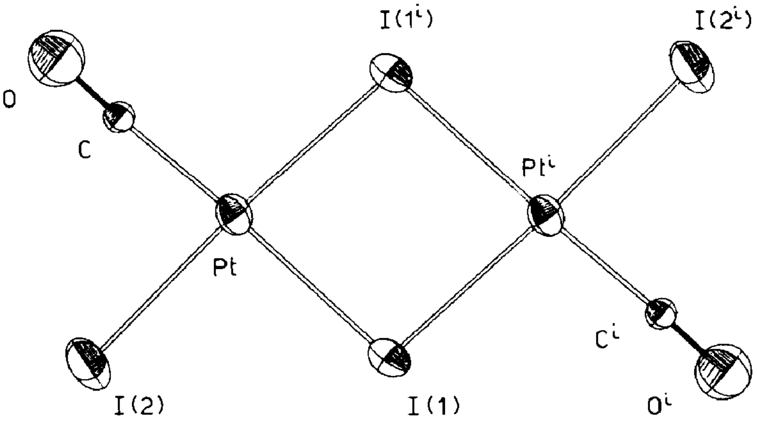

Fig. 1. A perspective ORTEP view of $Pt_2I_4(CO)_2$ with the numbering scheme used.

relatively low partial pressure of CO present under these conditions. The overall stoicheiometry of $Pt_2I_4(CO)_2$ formation is shown in eq. 5.

$$2\ PtI_2 + 2\ CO \rightarrow Pt_2I_4(CO)_2 \tag{5}$$

X-Ray diffraction study of $Pt_2I_4(CO)_2$

In view of the interest in bonding properties of halocarbonyl complexes of platinum(II) and in view of the fact that no structural studies on unsubstituted halocarbonyl complexes of noble metals have been reported in the literature except for AuCl(CO) [19], it was decided to study the dimeric compound by X-ray diffraction methods. The structure consists of centrosymmetric bridged dimeric $Pt_2I_2(\mu\text{-}I)_2(CO)_2$ units, see Fig. 1. The angles subtended at the metal by the four donor atoms (see Table 3) range from 85.8 to 96.5°. The four ligands are nearly coplanar, the maximum displacement from the weighted mean plane being 0.12 Å for C. The platinum atom lies out of the coordination plane by only 0.040 Å. Because of symmetry requirements, the Pt_2I_2 bridging rhombus must be exactly planar. In other square planar complexes this is not necessarily the case. For example, in $Rh_2Cl_2(CO)_4$, the two essentially planar moieties intersect [20] at an angle of 124°.

Comparison can be made between our structural parameters and those reported [21] for the $Pt_2I_6^{2-}$ anion. Some points deserve comment. Firstly, the $Pt\text{–}I_b$

Table 3

Bond lengths (Å) and angles (deg) in $Pt_2I_4(CO)_2$.

Pt–I(1)	2.622(3)	Pt–I(1ⁱ) [a]	2.630(2)
Pt–I(2)	2.596(3)	Pt–C	1.88(3)
C–O	1.06(4)		
I(1)–Pt–C	177.2(8)	C–Pt–I(1ⁱ)	96.5(8)
I(2)–Pt–I(1ⁱ)	176.1(1)	I(1ⁱ)–Pt–I(1)	85.8(1)
I(1)–Pt–I(2)	90.7(1)	Pt–I(1)–Ptⁱ	94.2(1)
I(2)–Pt–C	87.0(8)	Pt–C–O	177 (3)

[a] $i = \bar{x}, \bar{y}, \bar{z}$.

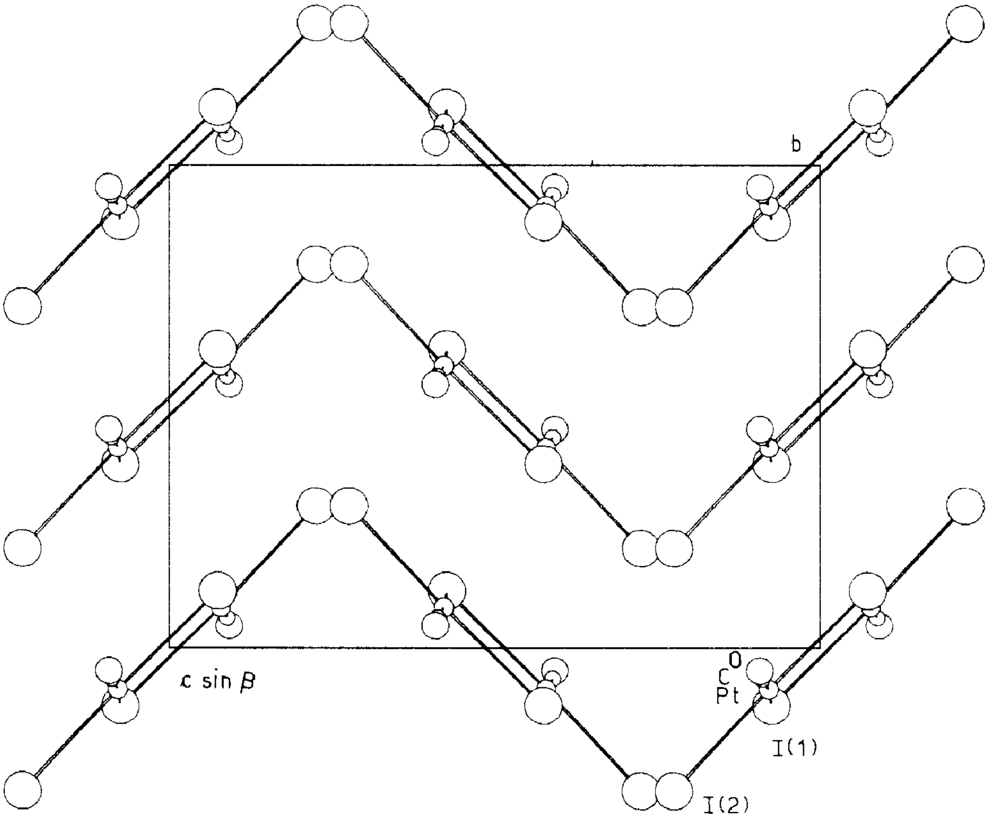

Fig. 2. Projection of the structure of $Pt_2I_4(CO)_2$ down the *a* axis.

(I_b = bridging iodide) distances are slightly longer than the corresponding Pt–I_t (I_t = terminal iodide) distances. The difference between the mean Pt–I_b distance (2.626 Å) and the Pt–I_t distance is 0.030 Å, which is consistent with the difference observed [22] for the iridium(III) complexes $Ir_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}I)_2I_2$. Secondly, the angles at platinum and at the iodide ligands within the bridge in $Pt_2I_4(CO)_2$ are similar to those in the $Pt_2I_6{}^{2-}$ anion [21], and the Pt...Pt non-bonding distances are 3.846 and 3.793 Å, respectively.

The crystal packing involves parallel dimers arranged in layers perpendicular to the $c^\star$ axis; the separation between the layers is $c/2$. On opposite sides of the coordination square, there are two atoms from adjacent dimers that interact weakly with the metal (Pt...I(2), ($\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$), 3.560 Å; Pt...C, ($\frac{1}{2}-x$, $-\frac{1}{2}-y$, $\bar{z}$), 3.814(3) Å; I(2)–Pt–C, 169.6°). A Pt...Pt axial interaction can therefore be excluded. The dimers in adjacent layers are inclined at about 90° (see Fig. 2).

The structural parameters for $Pt_2I_4(CO)_2$ (the centrosymmetric C_{2h} structure is expected to give rise to one CO stretching vibration (B_u) only] provide support for the earlier assignment [9] of a similar structure to $Pd_2Cl_4(CO)_2$ [9].

^{13}C *NMR and IR data; correlation with σ-bonding properties*

The CO stretching absorptions in the IR and the ^{13}C NMR data obtained by us and by others for these species are relevant to the discussion of the relative stabilities of halocarbonyl complexes of platinum(II) as a function of the halide. The

Table 4

^{13}C NMR spectra of halo carbonyl complexes of platinum(II) and platinum(IV) [a]

Compound	Chemical shift [b]	$J(^{195}Pt-^{13}C)$ (Hz)	Medium
cis-$PtCl_2(CO)_2$ [c]	152.0	1569.0	$CH_2Cl_2 + CD_2Cl_2$
	152.3	1580.1	*sym*-$C_2H_2Cl_4 + CD_2Cl_2$
	152.1	1586.2	$SOCl_2 + CD_2Cl_2$
cis-$PtBr_2(CO)_2$ [d]	152.5	1563.1	$CH_2Cl_2 + CD_2Cl_2$
cis-$PtI_2(CO)_2$	153.5	1521	benzene-d_6
	153.6	n.d.	$CH_2Cl_2 + CD_2Cl_2$ [e]
trans-$PtCl_2(CO)_2$	156.9	1564.6	$SOCl_2 + CDCl_3$
trans-$PtBr_2(CO)_2$	152.1	1573.5	$CH_2Cl_2 + CD_2Cl_2$ [e]
trans-$PtI_2(CO)_2$	163.6	1469.7	benzene-d_6
	163.3	1463.4	$CH_2Cl_2 + CD_2Cl_2$ [e]
$Pt_2Cl_4(CO)_2$	139.9	1958.8	$SOCl_2 + CDCl_3$
$[PtCl_5(CO)]^-$ [f]	161.4	1267	$SOCl_2 + CD_2Cl_2$

[a] Measured at room temperature, unless otherwise stated. [b] Downfield positive chemical shifts in ppm from TMS were measured from the central peak of the lock signal, to which a value obtained from the literature [23a] was assigned. [c] Reference 10 reports values of 151.6 ppm and 1576 Hz for the chemical shift and the coupling constant, respectively, for this compound. [d] Reference 10 reports values of 152.0 ppm and 1566 Hz for the chemical shift and the coupling constant, respectively, of this compound. [e] Measured at 0 °C in order to have a sufficiently high p(CO) and thus stabilize the monomer $PtI_2(CO)_2$, or to prevent isomerization in the case of *trans*-$PtBr_2(CO)_2$. [f] Reference 28 reports 1225 Hz for the coupling constant of $[PtBr_5(CO)]^-$ in $CH_2Cl_2 + CD_2Cl_2$.

data are given in Tables 2 and 4, respectively. The general trend, noted earlier [10], is that $\tilde{\nu}$(CO) decreases as the atomic number of the halide increases. The change is larger on going from bromide to iodide than from chloride to bromide. A specific solvent effect is evident from the data in Table 2: the $\tilde{\nu}$(CO)'s are shifted to higher values in chlorinated solvents such as dichloromethane and *sym*-tetrachloroethane. In this connection, it should be noted that $Pt_2Cl_4(CO)_2$ gives two ^{195}Pt resonances, attributed [1a] to two differently solvated species in $SOCl_2$.

The ^{13}C NMR data of Table 4 confirm the previously reported observations [10] that J(Pt–C) decreases in the sequence Cl > Br > I. Furthermore, consideration of the series of platinum(II) carbonyl derivatives for which the ^{13}C NMR data are now available shows that the values of J(Pt–C) decrease in the sequence $Pt_2X_4(CO)_2 > [PtX_3(CO)]^- >$ *cis*-$PtX_2(CO)_2 \geq$ *trans*-$PtX_2(CO)_2$. It therefore appears that the main factors responsible for the observed trends of coupling costants are: (a) the electronegativity of the halide within each presumably isostructural series, and, (b) the number of halides per platinum on going from one series to the next one.

It will be noted that halides give rise to the same sequence in J(C–H) values for halocarbon compounds [23], for J(Pt–P) values for both *trans*- and *cis*-$PtX_2(PBu_3)_2$ complexes [24], and, to a lesser extent, for values of J(Pt–H) for $PtX(Me)(PPh_3)_2$ complexes [25]. According to the accepted theoretical treatment [23], each coupling constant is dominated by the so-called Fermi contact term and, within the limits of the approximation used, the coupling constant has been related to the strength of the σ-bond connecting the two nuclei. We thus assume that a larger J(Pt–C) value is associated with a stronger Pt–C σ-bond. It will be noted that most of the $\tilde{\nu}$(CO) frequencies shown in Table 2 are close to or higher than the value for CO itself (2143 cm^{-1} [26]). The decrease of the $\tilde{\nu}$(CO)'s in the sequence Cl > Br > I is consistent with the variation of the NMR J parameter, once it is assumed that the σ-component predominates in the Pt–CO bond. A correspondingly lower transfer of electron density along the $Cl > Br > I$ sequence from the 5σ orbital of CO (which has a weak anti-bonding character [27]) will produce the observed effect.

Acknowledgement

The authors thank the Consiglio Nazionale delle Ricerche (C.N.R., Roma), Progetto Finalizzato di Chimica Fine e Secondaria for financial support. Thanks are due to the NMR Service of Area della Ricerca, Consiglio Nazionale delle Ricerche, Montelibretti, Roma, for the use of NMR facilities.

References

1 (a) D. Belli Dell'Amico, F. Calderazzo, C.A. Veracini, N. Zandonà, Inorg. Chem., 23 (1984) 3030. 4781; (b) T. Ziegler, V. Tschinke, C. Ursenbach, J. Am. Chem. Soc., 109 (1987) 4825.
2 D. Belli Dell'Amico, F. Calderazzo, N. Zandonà, Inorg. Chem., 23 (1984) 137.
3 D. Belli Dell'Amico, F. Calderazzo, G. Pelizzi, Inorg. Chem., 18 (1979) 1165.
4 L. Malatesta, L. Naldini, Gazz. Chim. Ital., 90 (1960) 505.
5 J.A. Connor, Topics Curr. Chem., 71 (1977) 71.
6 P. Schützenberger, Bull. Soc. Chim. Fr., 14 (1870) 97.
7 L. Romberg, Z. Anorg. Allg. Chem., 83 (1913) 36.
8 D. Belli Dell'Amico, F. Calderazzo, Gazz. Chim. Ital., 109 (1979) 99.
9 F. Calderazzo, D. Belli Dell'Amico, Inorg. Chem., 20 (1981) 1310.
10 J. Browning, P.L. Goggin, R.J. Goodfellow, M.G. Norton, A.J.M. Rattray, B.F. Taylor, J. Mink, J. Chem. Soc., Dalton Trans., (1977) 2061.
11 International Tables for X-ray Crystallography, Kynoch Press, Birmingham, 1974, Vol. 4, p. 99–101 and 149–150.
12 G.M. Sheldrick, SHELX-76. A Program for Crystal Structure Determination, University of Cambridge, 1976.
13 C.K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, 1976.
14 W.D.S. Motherwell, PLUTO, University of Cambridge, 1976.
15 F. Mylius and F. Foerster, Ber., 24 (1891) 2424.
16 D.R. Stull, E.F. Westrum and G.C. Sinke, The Chemical Thermodynamics of Organic Compounds, J. Wiley, New York, 1973.
17 The *trans*-geometry is the preferred one for $PtI_2(C_5H_5N)_2$ [18], in which the Pt–I bond distance is 2.597(1) Å, very close to that in $Pt_2I_4(CO)_2$.
18 G. Thiele, D. Wagner, Chem. Ber., 111 (1978) 3162.
19 M.G. Jones, Z. Naturforsch. B, 37 (1982) 823.
20 L.F. Dahl, C. Martell, D.L. Wampler, J. Am. Chem. Soc., 83 (1961) 1761.
21 R.D. Rogers, H. Isci and W.R. Mason, J. Cryst. Spectr. Res., 14 (1984) 383.
22 M.R. Churchill and S.A. Julis, Inorg. Chem., 18 (1979) 1215.
23 (a) J.B. Stothers, Carbon-13 NMR Spectroscopy, A Series of Monographs in Organic Chemistry, Vol. 24, Academic Press, New York, N.Y., 1972; (b) E. Shustorovich, Inorg. Chem., 18 (1979) 1039; (c) Y. Koie, S. Shinoda and Y. Saito, Inorg. Chem., 20 (1981) 4408.
24 (a) A. Pidcock, R.E. Richards and L.M. Venanzi, J. Chem. Soc. A, (1966) 1707; (b) L.M. Venanzi, Chem. Brit., (1968) 162.
25 C.D. Cook and K.Y. Wan, J. Am. Chem. Soc., 92 (1970) 2595.
26 J.B. Johnson and W.G. Klemperer, J. Am. Chem. Soc., 99 (1977) 7132.
27 R.S. Mulliken and W.C. Ermler, Diatomic Molecules, Academic Press, New York, N.Y., 1977.