

Journal of Organometallic Chemistry, 400 (1990) 303–320
 Elsevier Sequoia S.A., Lausanne
 JOM 21298

Organometallic derivatives of palladium, platinum, and gold

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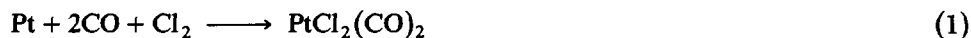
(Received August 14th, 1990)

Abstract

Information obtained in my and other research groups on halo carbonyls of palladium, platinum, and gold are surveyed. While for platinum(II), all the three halo (Cl, Br, I) complexes are well established both in solution and in the solid state for the $\text{PtX}_2(\text{CO})_2$, $\text{Pt}_2\text{X}_4(\text{CO})_2$ and $[\text{PtX}_3(\text{CO})]^-$ series, the bromo derivatives of palladium(II) and gold(I) are stable only in solution, under carbon monoxide. No evidence for the existence of iodo carbonyl derivatives of palladium(II) and gold(I) has been observed. The σ -component of the M–CO bond appears to predominate.

Introduction

The organometallic chemistry of group 10 (Ni, Pd, Pt) and group 11 elements (Cu, Ag, Au) has interested many researchers for several decades. Platinum has a leading historical position, since $\text{PtCl}_2(\text{CO})_2$ [1] and $[\text{PtCl}_3(\text{CH}_2\text{H}_4)]^-$ [2] were the first carbonyl and olefin complexes, respectively, to be reported. Dicarbonyldichloroplatinum(II) was obtained by Schlützenberger in 1868 by treating platinum sponge with a stream of carbon monoxide and dichlorine at about 250 °C. The reaction temperature had to be kept within a narrow range in order to prevent the



formation of the dimeric complex $\text{Pt}_2\text{Cl}_4(\text{CO})_2$, formed reversibly as shown in equilibrium 2, which is favoured at high temperatures. It should be noted that this



synthetic approach requires the use of CO and Cl_2 , which is a thermodynamically unstable system with respect to its conversion into COCl_2 , see equation 3. This point will be considered again later.



In addition to these organometallic derivatives of platinum(II), another compound of a group 10 element deserves a special attention, for both historical and

scientific reasons, namely $\text{Ni}(\text{CO})_4$. This was the first binary (or homoleptic) metal carbonyl derivative reported; its preparation dates back to 1890 [3] and the hundredth anniversary of its isolation was recently celebrated [4]. It is important to realize that $\text{Ni}(\text{CO})_4$ can be prepared directly from the components, according to equation 4. From a thermodynamic viewpoint, the process represented by equation 4 may be conveniently split into the two steps 4a and 4b, and, more generally, the formation of the tetracarbonyls of group 10 elements may be represented by steps 5a and 5b. However, the tetracarbonyls of palladium(0) and platinum(0) have not



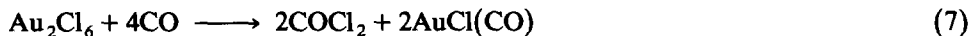
yet been isolated, although their presence in a matrix at low temperature has been established spectroscopically [5]. If it is assumed that $\text{Pd}(\text{CO})_4$ and $\text{Pt}(\text{CO})_4$ are thermodynamically unstable with respect to their components, an interesting problem is encountered in the case of palladium. While the relatively high enthalpy involved in the formation of $\text{Pt}_{(g)}$ (135 kcal/mol [6]) accounts for the instability of $\text{Pt}(\text{CO})_4$, this reasoning cannot be used for $\text{Pd}(\text{CO})_4$, since the enthalpy change for the formation of $\text{Pd}_{(g)}$ is only 91 kcal/mol [6], i.e. lower than that of nickel (103 kcal/mol). Thus, palladium must, to a first approximation, be assumed to be characterized by a rather low Pd-CO bond energy.

This and related problems stimulated our interest in this area of organometallic chemistry. At the beginning of our studies, the following compounds were well established in the literature: the halo complexes of platinum(II) $\text{PtX}_2(\text{CO})_2$, X = Cl [1], Br [7], and $\text{Pt}_2\text{X}_4(\text{CO})_2$, X = Cl, Br, I [8]; the chloro complexes of palladium(I), $[\text{Pd}_2\text{Cl}_4(\text{CO})_2]^{2-}$ [9] and $[\text{PdCl}(\text{CO})]_n$ [10]. In the case of gold, $\text{AuCl}(\text{CO})$ had been reported as early as 1925 [11]. Further points of interest were represented by: the absence of some of the compounds with the heavier halides (Br and I); the possibility of probing more deeply the nature of the metal-CO bond; the possibility of finding new and easier synthetic procedures; and the possibility of extending the study to the metal-olefin system, especially those of palladium and gold, which had been less studied than the corresponding platinum compounds.

Synthesis of gold- and platinum halo carbonyl compounds

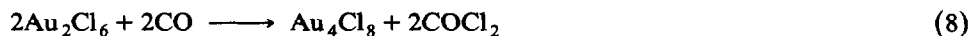
The experimental difficulties connected with the preparation of the chloro-carbonyls of platinum, associated with equilibrium 2, have been noted above. A further problem in dealing with halo-carbonyl complexes of gold and platinum is their high sensitivity to moisture. A real breakthrough in the preparation of these compounds came from the use of thionyl chloride as solvent. Anhydrous Au_2Cl_6 can be prepared simply by dehydration of the so-called tetrachloroauric acid as shown in eq. 6. Further reaction of the trichloride with carbon monoxide at atmospheric pressure and ambient temperature or slightly higher gave $\text{AuCl}(\text{CO})$ in

almost quantitative yields (see eq. 7) [12]. Reactions 6 and 7 require some H_3O^+ , $\text{AuCl}_4^- + \text{SOCl}_2 \longrightarrow 3\text{HCl} + \text{SO}_2 + 1/2\text{Au}_2\text{Cl}_6$ (6)



comments. Anhydrous gold(III) chloride can be prepared from the elements at 225–250°C [13]: this temperature is chosen as the best compromise between reasonable reaction rates and the requirement to minimize the thermal decomposition of the product to AuCl. Other preparative methods known at the time involved the treatment of gold metal with SO_2Cl_2 at 160°C [14] or with ICl [15]. It is of interest that the synthesis of Au_2Cl_6 described by Diemer [16], consisting of treating tetrachloroauric acid with dichlorine at about 200°C, was later [17] reported to give an impure product, mainly due to incomplete reaction. Dehydration of tetrachloroauric acid, as shown in equation 6 therefore appears to be the best way at present of making Au_2Cl_6 [18]. However, before reaction 7 was discovered, the reductive carbonylation of Au_2Cl_6 had been used to give AuCl(CO) both in the solid state [11] and in a solvent [19], though in low yields due to the use of relatively high temperatures necessary and the consequent decomposition of the product*. The main contribution to the driving force of reaction 7 comes from the strongly exothermic formation of COCl_2 : once an appropriate reaction pathway is found, use of the lowest possible temperature is therefore important in practice.

Some insight into the problem of the conversion of Au_2Cl_6 into AuCl(CO) by carbon monoxide came from observations carried out under conditions involving insufficient carbon monoxide: the black solid accidentally generated was systematically investigated and shown [21] to be mixed-valence halide of gold, Au_4Cl_8 , formed according to the stoichiometry of eq. 8. An X-ray diffraction study of a



twinned crystal of this compound showed it to have the chair-like structure depicted in Fig. 1. In this compound, there are two gold(III) and two gold(I) centres, with approximately square and linear coordination geometry, respectively. The gold(I) atoms are at a distance of 3.095(4) Å, which is close to the internuclear distance of 2.884 Å found [22] in the metal. The presence of a slight attractive interaction between the two gold(I) centres is supported by the observed Cl–Au–Cl angle, which is significantly smaller (175.1(5)°) than 180°, outside the eight-membered ring. Similar observations have been made with eight-membered ring systems containing gold(I) [23].

The preparation of the tetranuclear gold(III)–gold(I) species is now a readily reproducible procedure: the $\text{Au}_2\text{Cl}_6/\text{CO}$ system can be directed to produce Au_4Cl_8 almost exclusively, rather than AuCl(CO), simply by adjusting the amount of CO introduced initially (see eq. 8).

The preparation of AuCl(CO) from Au_2Cl_6 , as shown in eq. 7, is to be regarded as a reductive carbonylation of gold(III) in which carbon monoxide acts as both the reducing agent (being oxidized to COCl_2) and as a ligand for the metal in the lower oxidation state. A further insight into this process is provided by the detection [21a]

* Chlorocarbonylgold(I) can be sublimed in vacuo with extensive decomposition. The mass spectrum shows a low-intensity molecular ion peak [20].

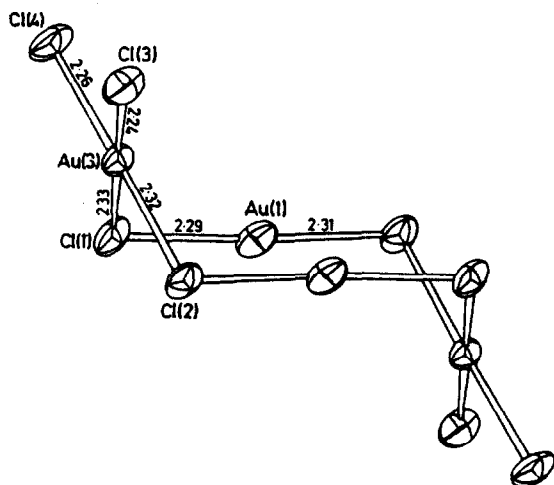


Fig. 1. Molecular structure of Au_4Cl_8 , reproduced with permission from the Royal Society of Chemistry [21b].

of the mixed-valence carbonyl complex formulated as $\text{Au}_2\text{Cl}_4(\text{CO})$, characterized by a CO stretching vibration (in thionyl chloride) at 2180 cm^{-1} , and first obtained by treating Au_2Cl_6 with $\text{AuCl}(\text{CO})$ (see eq. 9). It is a thermally unstable com-

$$\text{Au}_2\text{Cl}_6 + 2\text{AuCl}(\text{CO}) \longrightarrow 2\text{Au}_2\text{Cl}_4(\text{CO}) \quad (9)$$

pound, which was isolated only recently [24] by operating at about -33°C . The structure proposed [21a] for the mixed-valence carbonyl derivative is shown below together with its IR and ^{13}C NMR [24] data, along with the corresponding data for $\text{AuCl}(\text{CO})$. The shift of ca. 15 cm^{-1} in the carbonyl stretching vibration on going to $\text{Au}_2\text{Cl}_4(\text{CO})$ from $\text{AuCl}(\text{CO})$ is consistent with the increased average oxidation state of the metal.



$$\begin{aligned} \tilde{\nu}(\text{CO}) &= 2163\text{ cm}^{-1} \\ &(\text{SOCl}_2) \end{aligned}$$

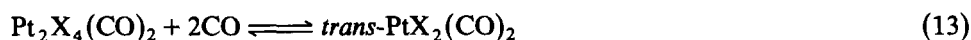
$$\begin{aligned} \tilde{\nu}(\text{CO}) &= 2180\text{ cm}^{-1} \\ &(\text{SOCl}_2) \end{aligned}$$

$$\begin{aligned} ^{13}\text{C NMR}: 171.8\text{ ppm (TMS)} & \quad ^{13}\text{C NMR}: 170.8\text{ ppm (TMS)} \\ (\text{CD}_2\text{Cl}_2, -50^\circ\text{C}) [24] & \quad (\text{CD}_2\text{Cl}_2, -50^\circ\text{C}) [24] \end{aligned}$$

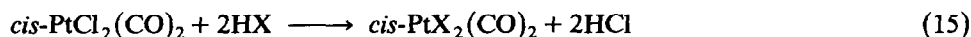
The knowledge acquired with the $\text{Au}_2\text{Cl}_6/\text{CO}$ system could only partially be used in the case of platinum. Dehydration of $(\text{H}_3\text{O}^+)_2\text{PtCl}_6^{2-}$ with thionyl chloride gave a platinum chloride of approximate composition PtCl_4 , which then underwent a slow reductive carbonylation to give *cis*- $\text{PtCl}_2(\text{CO})_2$. However, at room temperature and atmospheric pressure of CO long reaction times are needed for conversion of the kinetically inert Pt^{IV} species [25] into the halo-carbonyl complex [26]. Higher

rates were obtained by using higher temperatures and under CO pressure in toluene as solvent [27]. An alternative route to *cis*-PtCl₂(CO)₂ involves the use of a chlorinating agent on PtI₂(CO)₂ or on the iodo dimer Pt₂I₄(CO)₂ [28]. The iodide PtI₂, which is easily obtained [29] by treating PtCl₄²⁻ with I⁻, undergoes a smooth carbonylation to give PtI₂(CO)₂—almost exclusively the *trans* isomer—at atmospheric pressure of CO and at room temperature in toluene or in a chlorinated hydrocarbon solvent.

The most recent results on halo carbonyl complexes of platinum and their interconversions are summarized in the following sequence of reactions.



(X = Cl, Br)



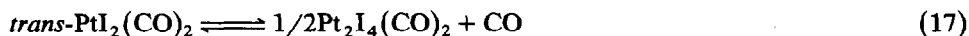
(X = Br, I [28])

Reaction 12 occurs with a number of chlorinating agents: the best at present available [30] is SO₂Cl₂ at room temperature. Recrystallization from toluene gives a satisfactory yield of *cis*-PtCl₂(CO)₂.

Finally, once an appropriate route to *cis*-PtCl₂(CO)₂ had been found, the corresponding bromo derivative was best prepared by the halide exchange shown in equation 15 [28], with HBr to supply the bromide ion. The complex *cis*-PtBr₂(CO)₂ can be obtained in this way, and so prior preparation of bromides of platinum is unnecessary. (Earlier preparations of *cis*-PtBr₂(CO)₂ required the use of the hexabromoplatinate anion [8] PtBr₆²⁻ at high CO pressure and high temperature of PtBr₂ [31], the latter being treated with CO at 220° C.) Halide exchanges similar to that shown in eq. 15 had been reported earlier [7] by Mylius and Foerster, who prepared Pt₂Br₄(CO)₂ from PtCl₂(CO)₂ and concentrated hydrobromic acid, presumably through the intermediacy of [PtBr₃(CO)]⁻. The exchange reaction 15 has interesting theoretical and practical features. In control IR spectrophotometric experiments carried out with the PtCl₂(CO)₂/HBr system, the exchange was found [28] to be complete at room temperature, the products of the reaction being HCl ($\tilde{\nu}(\text{H}-\text{Cl})$, 2740 cm⁻¹, compared with $\tilde{\nu}(\text{H}-\text{Br})$ of 2440 cm⁻¹ in the toluene used as solvent for the reaction), and *cis*-PtBr₂(CO)₂ ($\tilde{\nu}(\text{CO})$, 2162 and 2119 cm⁻¹ in toluene, compared with the corresponding bands of the chloro derivative at 2170 and 2126 cm⁻¹). The driving force for the occurrence of the exchange reaction (15) is believed to originate from the formation of HCl in solution; the available data in the literature relate to the free energy change ΔG° for HX in the gas phase [32] (-22.77, -12.73 and +0.39 kcal/mol, for X = Cl, Br, I, respectively).

In summarizing the preparative aspects of platinum(II) carbonyl complexes we note that a pivotal position is occupied by the iodo-carbonyl compound PtI₂(CO)₂ and its corresponding dimer Pt₂I₄(CO)₂. Through its intermediacy, all six halo carbonyl complexes of platinum(II), of both the monomeric and dimeric series,

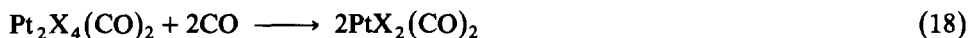
$\text{PtX}_2(\text{CO})_2$ and $\text{Pt}_2\text{X}_4(\text{CO})_2$, respectively, are available through reactions occurring at ambient temperature and pressure of carbon monoxide. Due to the special importance of the iodo carbonyls, the $\text{PtI}_2(\text{CO})_2/\text{Pt}_2\text{I}_4(\text{CO})_2$ system has been studied in detail [28]. Pure *trans*- $\text{PtI}_2(\text{CO})_2$ is difficult to be obtained for two main reasons: (a) it is in equilibrium in solution with small amounts of the corresponding *cis* isomer, see eq. 16; (b) it coexists with the dimer $\text{Pt}_2\text{I}_4(\text{CO})_2$, in a CO-dependent equilibrium (see eq. 17), which is readily attained both in solution and in the solid state.



The stability of $\text{PtX}_2(\text{CO})_2$ with respect to the corresponding dimers $\text{Pt}_2\text{X}_4(\text{CO})_2$ decreases in the sequence $\text{Cl} > \text{Br} > \text{I}$. Thus the iodo dimer $\text{Pt}_2\text{I}_4(\text{CO})_2$ can be obtained pure [33] simply by carrying out the carbonylation of PtI_2 in a solvent such as dichloromethane or *n*-pentane, the relatively high vapour pressure of which keeps the partial pressure of CO low, as required to shift equilibrium 17 to the right.

Carbonylation of halide-bridged systems of gold and platinum

In the preceding section it has been shown that the monomeric halo carbonyls of platinum(II) can be obtained by the carbonylation of the $\text{Pt}_2\text{X}_4(\text{CO})_2$ dimers (see eq. 18). In this section, an attempt will be made to examine this reaction in more detail, in comparison with the strictly analogous carbonylation of AuCl to AuCl(CO) (see eq. 19) reported in 1930 [19]. These reactions can be described ap-



propriately under a common heading in view of the solid-state- and solution structures of the starting materials. The solid-state structure of $\text{Pt}_2\text{I}_4(\text{CO})_2$ has been studied by X-ray diffraction and found [28] to consist of bridged dimeric $\text{Pt}_2\text{I}_2(\mu\text{-I})_2(\text{CO})_2$ units, as shown in Fig. 2. In the molecule each platinum atom attains its usual square-planar coordination, being bonded to two bridging iodides, a terminal

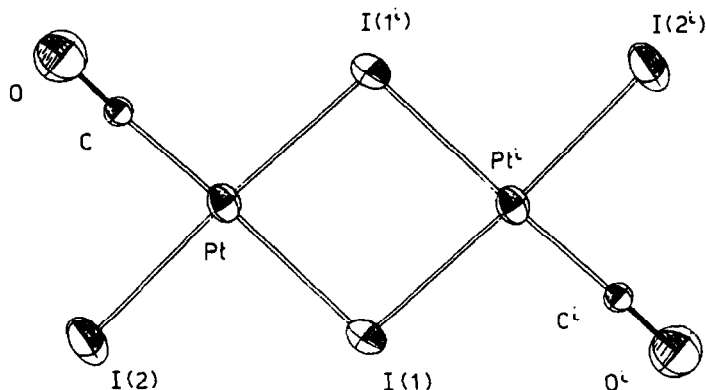


Fig. 2. The molecular structure of $\text{Pt}_2\text{I}_4(\text{CO})_2$ [28].

iodide, and the carbon atom of the carbon monoxide group. The platinum atom lies out of the coordination plane by only 0.040 Å, and symmetry requirements constrain the Pt₂I₂ rhombus to be exactly planar. The Pt...Pt nonbonding contact in the dimer is 3.846(2) Å.

The Pt-I_b distance of 2.622(3) Å is only slightly longer than the Pt-I_t distance of 2.596(3) Å. Similarly, in the Pt₂I₆²⁻ anion [34], the difference between the Pt-I_b and the Pt-I_t bond distances is about 0.030 Å, which is consistent with the similar difference found [35] for the iridium(III) complexes with halide bridges Ir₂(η⁵-C₅Me₅)₂(μ-I)₂I₂. It has already been pointed out that the (M-X_b) - (M-X_t) values decrease in the Cl > Br > I sequence. A similar trend can be seen for platinum(II) by comparing the data [34] for the Pt₂I₆²⁻ anion with those for the corresponding chloro- [36] and bromo [37] derivatives. In these compounds, the differences (Pt-X_b) - (Pt-X_t) are +0.055, +0.029 and -0.012 for X = Cl, Br, and I, respectively.

The centrosymmetric molecular structure of C_{2h} symmetry, found for Pt₂I₄(CO)₂, for which only one IR active CO stretching vibration (B_u) is expected, is maintained in solution. This can be seen by comparing the IR carbonyl stretching vibrations of the dimeric halo complexes of platinum(II) (see Table 1) with those of the monomeric compounds PtX₂(CO)₂, in this case for both the *cis* and *trans* isomers. With this information at hand, it is now possible to discuss reactions 18 and 19, taking into account that the solid-state structure of AuCl [38] consists of zig-zag chloride-bridged chains with the expected linear coordination around gold. Relevant to the discussion are the molecular structures of the monomeric PtX₂(CO)₂ and AuCl(CO) complexes, which were determined by IR and X-ray methods, respectively. Table 1 shows that *cis*-PtX₂(CO)₂ gives two IR CO stretching vibrations, as expected for a monomeric structure of C_{2v} symmetry. For AuCl(CO), an X-ray study has shown [39] that it is mononuclear with a substantially linear coordination around gold and, most interestingly, with intermolecular Au...Cl contacts of 3.38 Å.

In all cases, reactions 18 and 19 are completely shifted towards the monomeric platinum(II) carbonyl complexes at room temperature under CO at atmospheric pressure (*p*(CO) + vapour pressure of the solvent). It is important to appreciate what changes are involved in the transformation from Pt₂X₄(CO)₂ to PtX₂(CO)₂,

Table 1

IR carbonyl stretching vibrations of halo carbonyl complexes of platinum(II) (cm⁻¹)

| Compound | n-heptane | toluene | <i>sym</i> -C ₂ H ₂ Cl ₄ ^a | Reference |
|---|-------------------|-------------------|--|-----------|
| <i>cis</i> -PtCl ₂ (CO) ₂ | 2167,2120 | 2170,2126 | 2179,2136 | 28 |
| <i>cis</i> -PtBr ₂ (CO) ₂ | 2156,2115 | 2162,2119 | 2170,2130 | 28 |
| <i>cis</i> -PtI ₂ (CO) ₂ | 2143 ^b | 2147 ^b | 2151 | 28 |
| <i>trans</i> -PtCl ₂ (CO) ₂ | | | 2150 ^c | 45 |
| <i>trans</i> -PtBr ₂ (CO) ₂ | 2136 | 2136 | 2142 | 28 |
| <i>trans</i> -PtI ₂ (CO) ₂ | 2122 | 2121 | 2126 | 28 |
| Pt ₂ Cl ₄ (CO) ₂ | 2130 | 2128 | 2136 | 28 |
| Pt ₂ Br ₄ (CO) ₄ | 2122 | 2119 | 2127 | 28 |
| Pt ₂ I ₄ (CO) ₂ | 2106 | 2104 | 2110 | 28 |

^a The bromo- and iodo derivatives were shown not to undergo halide exchange in *sym*-tetrachloroethane at room temperature, but exchange did occur in thionyl chloride. ^b Band around 2110 cm⁻¹ partially covered by the absorption due to *trans*-PtI₂(CO)₂. ^c Measured in thionyl chloride.

which, as already mentioned, is, thermodynamically favourable overall in spite of the unfavourable entropy term. This transformation requires the cleavage of two bonds between platinum and a bridging halide, $\text{Pt}-\text{X}_b$, and their replacement by two new bonds, namely $\text{Pt}-\text{CO}$ and $\text{Pt}-\text{X}_t$. Thus, the $\text{Pt}-\text{CO}$ bond appears to be reasonably strong, if one takes into consideration that the $\text{Pd}-\text{Cl}_t$ and $\text{Pd}-\text{Cl}_b$ bond energies have been estimated [40] to be 62 and 48 kcal/mol, respectively, and $\text{Pt}-\text{X}$ bonds are believed [41] to be stronger than $\text{Pd}-\text{X}$ bonds. Unfortunately, an estimate of the $\text{Pt}-\text{CO}$ bond energy cannot be given, because of the uncertainty about the $\text{Pt}-\text{Cl}$ bonds. This point will be discussed again below, in connection with the halo carbonyl complexes of palladium(II).

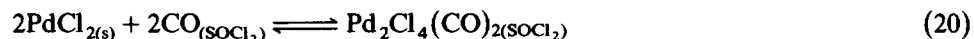
The situation is substantially similar in the transformation shown in eq. 19 of the polynuclear AuCl into $\text{AuCl}(\text{CO})$, in that the bonding situation $\text{Cl}_b-\text{Au}-\text{Cl}_b$ is converted into the new one, $\text{Cl}_t-\text{Au}-\text{CO}$. Relevant to this discussion is also the evaluation of the entropy term involved in the reaction of eq. 19. At 298 K, the $T\Delta S$ term must correspond to about 9 kcal/mol according to determinations carried out during the study of equilibria involving the coordinative addition of carbon monoxide [42]. As far as the $\text{Au}-\text{Cl}$ bond energy is concerned, some information about it can be obtained from the $\text{Au}-\text{Cl}$ diatomic molecule [43] ($D_{298}^\circ = 82 \pm 2.3$ kcal/mol). By further assuming that the difference between the $\text{Au}-\text{Cl}_t$ and $\text{Au}-\text{Cl}_b$ bond energies is the same as that reported [40] for palladium, the $\text{Au}-\text{CO}$ bond energy can be calculated to be about 50 kcal/mol by taking into account that unfavourable entropy term in the carbonylation may be compensated by the favourable entropy contribution arising from the fragmentation of the $(\text{AuCl})_n$ solid-state extended structure. This value should be compared with the usually accepted $\text{M}-\text{CO}$ bond energies for $5d$ transition elements [44].

Equations 13 and 14 depict the transformation of the dimeric platinum(II) halo complexes to the corresponding monomers. The study of the reaction of $\text{Pt}_2\text{Cl}_4(\text{CO})_2$ with carbon monoxide allowed us to detect the intermediate *trans*- $\text{PtCl}_2(\text{CO})_2$ [45] formed on the way to the *cis* isomer. From the mechanistic viewpoint, the initial formation of the *trans* isomer is expected in view of the strong *trans* effect of the CO ligand in the dimeric centrosymmetric structure of the $\text{Pt}_2\text{X}_4(\text{CO})_2$ starting product. The *trans* compounds can be observed spectroscopically (see Table 1), for $\text{X} = \text{Cl}, \text{Br}$, through their unique CO stretching vibration, as expected for their D_{2h} symmetry. However, with a relatively small activation energy they can be converted either back to the dimer or to the thermodynamically more stable *cis* isomer. It is also of interest to consider the monomer \rightleftharpoons dimer equilibrium, i.e. the reverse of eq. 18, as a function of the halide ligand. Although in our hands, *cis*- $\text{PtCl}_2(\text{CO})_2$ was found to be stable in refluxing thionyl chloride (b.p. 746 mmHg, 78.8°C), we confirmed the earlier finding [8] that conversion into the dimer occurs in refluxing benzene (b.p. 760 mmHg, 80.1°C); the bromo derivative gives the dimer at the reflux temperature of n-hexane, and the iodo compound is almost completely converted into the dimer even at room temperature under a reduced partial pressure of CO. The comparison between the chloro and the bromo derivatives is significant, since the experiments were carried out under similar conditions of low partial pressure of CO, i.e. at the boiling point of the solvent. In view of the fact that the formation of the dimer presumably proceeds via a dissociative mechanism, the observed trend in reactivity may be taken as an evidence for increase in the $\text{Pt}-\text{CO}$ bond strength in the sequence $\text{Br} < \text{Cl}$.

As noted above, *trans*-PtI₂(CO)₂ is the predominant species in solution. This observation does not assist in speculation about the nature of the Pt–CO bond in combination with iodide, since steric effects due to the bulk of the iodide could account for the observed geometry in solution. It is noteworthy, in this connection, that the *trans* geometry is preferred in PtI₂(C₅H₅N)₂ also [46], which has a Pt–I bond length of 2.597(1) Å, substantially identical to the Pt–I_i bond length in the Pt₂I₄(CO)₂ dimer. It can be suggested, however, that no overwhelming π -back bonding effects operate within the Pt–CO system in PtI₂(CO)₂, since they should favour the *cis* isomer.

The palladium–CO system

A compound of composition PdCl₂(CO) was reported [47] by Manchot and König, and was obtained by carbonylation of PdCl₂ in methanol; this formulation was later questioned [48] and the product suggested to be a chloro carbonyl of palladium(I) contaminated with PdCl₂. An IR carbonyl stretching band had been observed [49] at 1976 cm⁻¹ for the product obtained in the way described by Manchot and König, but this frequency appeared to be unusually low for this type of compound in comparison, for example, with absorptions typical of the corresponding complexes of platinum(II) of similar stoichiometry (see Table 1). It was therefore of interest to attempt a completely new synthesis of the chloro carbonyl of palladium(II) by using carbonylation in thionyl chloride that had proved so successful in the case of the carbonyl derivatives of gold(I) and platinum(II). This offered the possibility of clarifying some conflicting literature reports and, at the same time, studying in more detail a system of some relevance in catalysis [50]. It was found [51] that PdCl₂ is carbonylated to Pd₂Cl₄(CO)₂, according to eq. 20. Under these



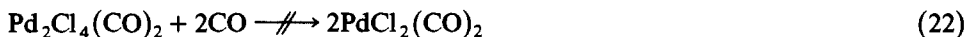
conditions, no reduction to palladium(I) occurs. The reaction is exothermic ($\Delta H^\circ = -13.6 \pm 0.2$ kcal/mol), according to a subsequent study [51b] of equilibrium 20 at variable temperature. The equilibrium is therefore favoured by relatively lower temperatures and, of course, by high CO partial pressures: a 0.5 M solution of the dimeric carbonyl can be readily obtained at 50°C at a pressure of CO of about 5 atm. The K_{eq} -temperature relationship is shown in eq. 21 and the thermodynamic parameters of reaction 20 were used to obtain some information about the

$$-\ln K = -6834/T + 15.4 \quad (21)$$

Pd–CO bond energy. By making some necessary assumptions the Pd–CO bond energy was estimated to be about 24 kcal. This value compares satisfactorily, with, for example, the Fe–CO bond energies of 15.3 and 17.5 kcal mol⁻¹ calculated [44] for FeBr₂(CO)₄ and FeI₂(CO)₄, respectively, when account is taken of the fact that the strength of a metal–CO bond increases on going from a 3*d* to a 4*d* element. Average metal–CO bond energies in metal carbonyls (with a zero oxidation state of the central atom) range from 24 kcal in Mn₂(CO)₁₀ to 35 kcal in Ni(CO)₄, while for 4*d* elements, in the same oxidation state the values range from 36.3 kcal in Mo(CO)₆ to 41 kcal in Ru₃(CO)₁₂. An estimate of 25 kcal mol⁻¹ has been made for the Pd–CO bond energy [44]. The agreement with the value of 24 kcal estimated for the PdCl₂/CO system, if it is real, is impressive, since we are dealing with systems in different oxidation states. We return to this point later below.

In view of the special features of reaction 20, isolation of the dimeric $\text{Pd}_2\text{Cl}_4(\text{CO})_2$ required some special precaution: the yellow-orange microcrystalline compound must be precipitated from thionyl chloride by addition of carefully pre-dried n-heptane, then filtered off and dried in a stream of carbon monoxide. In thionyl chloride, i.e. under strictly anhydrous conditions, a $2.2 \times 10^{-2} M$ solution of the compound is stable at atmospheric pressure of CO at 35°C . However, upon contact with trace amounts of water in an organic solvent the palladium(II)-carbonyl complex decomposes immediately, with formation of an unidentified black material, presumably palladium metal. The compound shows a single CO stretching vibration, at 2159 cm^{-1} , in cyclohexane, which can be compared with the band of the corresponding platinum(II) dimer at 2128 cm^{-1} in the same solvent [51].

In the studying of the system $\text{PdCl}_2/\text{CO}/\text{Pd}_2\text{Cl}_4(\text{CO})_2$, several temperatures and pressures were used, but no evidence was found of the existence of a monomeric carbonyl derivative of palladium(II) in contrast to the situation for platinum. In other words, reaction 22 does not proceed to any detectable extent. This is an indirect confirmation of the 24 kcal estimated for the Pd-CO bond energy, as outlined above. In fact, taking into consideration the accepted values [40] of Pd-Cl_b and Pd-Cl_t bond energies of 48 and 62 kcal, respectively, a simple calculation shows that the Pd^{II}-CO_t bond energy should be about 34 kcal for the enthalpy change of equation 22 to become approximately zero and for the palladium(II)-carbonyl monomeric complex to become observable.



A comparison of the CO stretching vibrations for platinum(II) and palladium(II) carbonyl complexes is presented in Table 2. It is evident that in all cases the palladium(II) complexes are characterized by a higher frequency of the carbonyl stretching band by about 30 cm^{-1} . Moreover, for the neutral species, the wavenumber value of coordinated CO is well above that reported for CO in the gas phase [43] (2143 cm^{-1}). In the usually accepted model of σ - π synergic effects this would correspond to a negligible degree of π -back donation.

In connection with the discussion of the failure to observe the product of equilibrium 22, it is noteworthy that dicarbonyl derivatives of palladium(II) have been synthesized containing perhalogenated phenyl groups instead of halides, namely $\text{Pd}(\text{C}_6\text{F}_5)_2(\text{CO})_2$ and $\text{Pd}(\text{C}_6\text{Cl}_5)_2(\text{CO})_2$ [52].

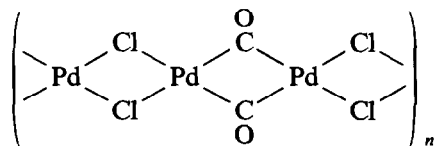
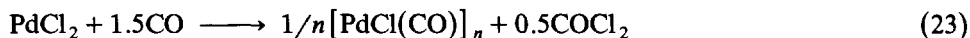
Table 2

The IR carbonyl stretching vibrations for halo carbonyl of palladium(II) and platinum(II)

| Compound | $\bar{\nu}(\text{CO}) (\text{cm}^{-1})$ | Solvent | Ref. |
|---------------------------------------|---|--|------|
| $\text{Pd}_2\text{Cl}_4(\text{CO})_2$ | 2160 | Toluene | 51 |
| $\text{Pt}_2\text{Cl}_4(\text{CO})_2$ | 2128 | Toluene | 28 |
| $[\text{PdCl}_3(\text{CO})]^-^a$ | 2132 | CH_2Cl_2 | 60 |
| $[\text{PtCl}_3(\text{CO})]^-^b$ | 2098 | CH_2Cl_2 | 28 |
| $[\text{PdBr}_3(\text{CO})]^-^a$ | 2120 | CH_2Cl_2 | 60 |
| $[\text{PtBr}_3(\text{CO})]^-^a$ | 2089 | CH_2Cl_2 | 28 |
| $[\text{PdI}_3(\text{CO})]^-^a$ | 2105 | <i>sym</i> - $\text{C}_2\text{H}_2\text{Cl}_4$ | 60 |
| $[\text{PtI}_3(\text{CO})]^-^a$ | 2078 | ^c | 28 |

^a Tetra-n-butylammonium derivative. ^b Tetra-n-propylammonium derivative. ^c In dichloromethane.

In contrast with the $\text{Au}_2\text{Cl}_6/\text{CO}$ system, in which carbon monoxide can be oxidized to COCl_2 , no reduction of palladium(II) to palladium(I) or palladium(0) was observed when thionyl chloride was used as the reaction medium (see eq. 20). However, when acetic anhydride was used as medium, reduction did occur, with formation of the polynuclear palladium(I) species $[\text{PdCl}(\text{CO})]_n$ [51b]. The overall reaction stoichiometry may be represented as in eq. 23, the phosgene produced presumably being consumed by acetic anhydride to give CH_3COCl and CO_2 [53]. The yields of isolated palladium(I) compound are as high as 90%, and the product is characterized by a carbonyl stretching vibration at 1975 cm^{-1} , in agreement with earlier [10] findings for the same compound obtained by a different route. Furthermore, treatment of the polynuclear species with $[\text{NH}_2\text{Et}_2]\text{Cl}$ in *sym*-tetrachloroethane gave the previously known [9] $[\text{Pd}_2\text{Cl}_4(\text{CO})_2]^{2-}$, characterized by a CO stretching vibration at 1916 cm^{-1} in that solvent. It will be seen that lowering of the oxidation state from II to I lowers the CO stretching vibration by almost 200 cm^{-1} for the neutral species on going from $\text{Pd}_2\text{Cl}_4(\text{CO})_2$ to $[\text{PdCl}(\text{CO})]_n$. Such a large decrease is attributable to the presumably large change in structure. The anionic $[\text{Pd}_2\text{Cl}_4(\text{CO})_2]^{2-}$ has been shown [9] to be unique in that it has *bridging carbonyl groups* rather than chloride bridges. If the same type of structure also holds for the neutral palladium(I) species, the latter may be suggested to have a polynuclear structure with both chloride and carbon monoxide bridges, as shown below. In such a case, the electron-count for the d^9 palladium(I) would be 15 (taking no account of the possible spin-pairing due to the metal-metal bond), i.e. the same as that in the dinuclear anionic species. In the latter, the alternative chloride-bridged structure, not observed experimentally, would bring the central metal atom to an electron-count of 17, an apparently less favourable situation for palladium.



Additional spectroscopic data on halo carbonyl complexes of platinum(II) and platinum(IV)

In relation to the discussion of the relative stabilities of halo carbonyl complexes of platinum(II), to be used later in considering the same question for palladium(II), the ^{13}C NMR data in Table 3 are important as well as the values of IR carbonyl stretching vibrations shown in Tables 1 and 2. In Table 3, both the chemical shifts and the $J(\text{Pt}-\text{C})$ coupling constants are given. Several observations emerge from consideration of the data. First, our data confirm the trends in $J(\text{Pt}-\text{C})$ that had been reported earlier [54], see Table 4, for some of the series including iodides, as a function of the bonded halide, namely that the coupling constant decreases in the sequence $\text{Cl} > \text{Br} > \text{I}$. By taking into account of other available data for coupling constants for platinum complexes, it can be seen that a similar effect of the halide ligand can be recognized for other NMR-active nuclei. For example, for the series of *trans*- and *cis*- $\text{PtX}_2(\text{PBU}_3)_2$ complexes [55] reported by Venanzi and coworkers, the

Table 3

¹³C NMR spectra of carbonyl complexes of platinum(II) and platinum(IV) ^a

| Compound | Chemical shift ^b | $J(^{195}\text{Pt}-^{13}\text{C})$ (Hz) | Medium | Ref. |
|--|-----------------------------|---|---|------|
| <i>cis</i> -PtCl ₂ (CO) ₂ ^c | 152.0 | 1569.0 | CH ₂ Cl ₂ + CD ₂ Cl ₂ | 28 |
| | 152.3 | 1580.1 | <i>sym</i> -C ₂ H ₂ Cl ₄ + CD ₂ Cl ₂ | 28 |
| | 152.1 | 1586.2 | SOCl ₂ + CD ₂ Cl ₂ | 28 |
| <i>cis</i> -PtBr ₂ (CO) ₂ ^d | 152.5 | 1563.1 | CH ₂ Cl ₂ + CD ₂ Cl ₂ | 28 |
| | 153.5 | 1521 | benzene- <i>d</i> ₆ | 28 |
| <i>cis</i> -PtI ₂ (CO) ₂ | 153.6 | n.d. | CH ₂ Cl ₂ + CD ₂ Cl ₂ ^e | 28 |
| | 156.9 | 1564.6 | SOCl ₂ + CDCl ₃ | 28 |
| <i>trans</i> -PtCl ₂ (CO) ₂ | 152.1 | 1573.5 | CH ₂ Cl ₂ + CD ₂ Cl ₂ ^e | 28 |
| <i>trans</i> -PtBr ₂ (CO) ₂ | 163.6 | 1469.7 | benzene- <i>d</i> ₆ ^e | 28 |
| <i>trans</i> -PtI ₂ (CO) ₂ | 163.3 | 1463.4 | CH ₂ Cl ₂ + CD ₂ Cl ₂ | 28 |
| | 139.9 | 1958.8 | SOCl ₂ + CDCl ₃ | 28 |
| Pt ₂ Cl ₄ (CO) ₂ | 161.4 | 1267 | SOCl ₂ + CD ₂ Cl ₂ | 28 |
| [PtCl ₅ (CO)] ⁻ | | | | |

^a Unless otherwise stated, the spectra were recorded at room temperature. ^b Downfield positive chemical shifts in ppm from TMS were measured from the central peak of the lock signal, to which the literature value [57] was assigned. ^c Reference 31 reports values of 151.6 ppm and 1576 Hz for the chemical shift and the coupling constants, respectively, of this compound. ^d Values of 152.0 ppm and 1566 Hz are reported for this compound in reference 31. ^e Determined at 0 °C to prevent loss of CO or isomerization. ^f Reference 59 gives a value of 1225 Hz for the coupling constant of [PtBr₅(CO)]⁻ in CH₂Cl₂ + CD₂Cl₂.

$J(\text{Pt}-\text{P})$ decrease along the series Cl > Br > I for both types of complex. Furthermore, a similar, though less substantial trend in $J(\text{Pt}-\text{H})$ can be seen from the data [56] for the platinum(II) complexes PtX(Me)(PPh₃)₂. According to current theory [57], the value of the coupling constant $J(\text{X}-\text{Y})$ between two nuclei X and Y is

Table 4

¹³C NMR data and coupling constants of organometallic compounds as a function of the halide

| Compound | Chemical shift ^a | Solvent | $J(\text{M}-^{13}\text{C})$ (Hz) | Ref. |
|---|-----------------------------|--------------------------------|----------------------------------|--------------|
| [<i>trans</i> -PtCl(PPh ₃) ₂ (CO)] ⁺ | 158.6 | | 1788 | 54 |
| [<i>trans</i> -PtBr(PPh ₃) ₂ (CO)] ⁺ | 159.0 | | 1772 | 54 |
| [<i>trans</i> -PtI(PPh ₃) ₂ (CO)] ⁺ | 157.4 | | 1658 | 54 |
| [PtCl ₃ (CO)] ⁻ | 152.0 | acetone- <i>d</i> ₆ | 1732 | 31 |
| [PtBr ₃ (CO)] ⁻ | 153.0 | acetone- <i>d</i> ₆ | 1701 | 31 |
| [PtI ₃ (CO)] ⁻ | 156.2 | acetone- <i>d</i> ₆ | 1636 | 31 |
| [WCl(CO) ₅] ⁻ | 198.7 | CDCl ₃ | 129 | ^b |
| [WI(CO) ₅] ⁻ | 197.1 | acetone- <i>d</i> ₆ | 127 | ^c |
| HgCl(Me) | 8.6 | CDCl ₃ | 1430.7 | ^d |
| HgBr(Me) | 12.8 | CDCl ₃ | 1393.6 | ^d |
| HgI(Me) | 18.8 | CDCl ₃ | 1801.3 | ^d |
| SnClEt ₃ | 9.3 | Neat liquid | 352 | ^e |
| SnBrEt ₃ | 9.0 | Neat liquid | 340 | ^e |
| SnIEt ₃ | 7.9 | Neat liquid | 326 | ^e |

^a Downfield positive chemical shift from TMS. ^b B.D. Dombek and R.J. Angelici, *J. Am. Chem. Soc.*, 98 (1976) 4110. ^c F.H. Köhler, H.J. Kalder and E.O. Fischer, *J. Organomet. Chem.*, 113 (1976) 11. ^d A.J. Grown, O.W. Howarth and P. Moore, *J. Chem. Soc., Dalton Trans.*, (1976) 1589. ^e T.N. Mitchell, *J. Organomet. Chem.*, 59 (1973) 189.

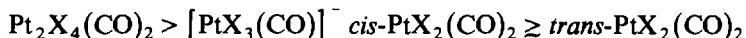
related, through the so-called Fermi contact term, to the s character of the hybrid used in bonding. Within the limits of the approximation used, the coupling constants have been related directly to the strength of the X–Y σ -bond. It can be seen that the effect of the halide ligand on $J(\text{X–Y})$ operates in the same direction for a large number of cases (see Table 4). Unfortunately, the data for typical transition elements are limited or not readily available and the discussion below therefore deals mainly with metal–carbon bonds for non-transition elements. Within mercury–alkyl derivatives, for which the coupling constants $J(\text{Hg–C})$ decrease in the sequence $\text{Cl} > \text{Br} > \text{I}$, thermochemical data are available to substantiate the assumption of a decreasing bond energy in the same direction. The Hg–Me dissociation energies [58] for $\text{HgX}(\text{Me})$ have been reported to be: 64.3 ± 2 , 61.8 ± 2 , and 59.0 ± 2 kcal mol⁻¹ for X = Cl, Br, and I, respectively. The values given for the $\text{HgX}(\text{Et})$ derivatives are: 60.3 ± 3 (Cl), 57.6 ± 3 (Br), and 53.7 ± 3 (I) kcal mol⁻¹. Although the estimated errors are large, a tendency for decrease of the Hg–C bond strength in the sequence $\text{Cl} > \text{Br} > \text{I}$ can be seen, and should be regarded as plausible, since other data (vide infra) point to the same trend. From now on, then, it will be assumed that a larger coupling constant $J(\text{Pt–C})$ is associated with a stronger Pt–C σ -bond.

This is an important conclusion, since we have now an independent parameter to use in discussing the earlier observation by Malatesta and Naldini [8] that in the series of platinum(II) halo carbonyl complexes the apparent thermal stability of the complexes increases in the sequence $\text{I} < \text{Br} < \text{Cl}$: this trend may be attributed to a progressively stronger Pt–C bond in that sequence. Of course, Pt–X bonds in halo carbonyl complexes of platinum(II) undergo hydrolysis more easily in the sequence $\text{I} < \text{Br} < \text{Cl}$: this may be due to both kinetic (higher polarity of Pt–X bond with the lighter halide) and thermodynamic (formation of the more stable HX with the lighter halide) factors.

As noted previously [55] for tertiary phosphine complexes of platinum(II), the effect of the halide ligand on the coupling constant is slightly larger for the *trans* $\text{PtX}_2(\text{CO})_2$ series than for the *cis* series. However, there is an important difference between the tertiary phosphine and the carbonyl complexes, the effect of the geometry on $J(\text{Pt–Y})$ being much larger for the tertiary phosphine derivatives. For example, in *cis*- and *trans*- $\text{PtX}_2(\text{CO})_2$, the coupling constants are similar (*cis*- $\text{PtCl}_2(\text{CO})_2$ has $J(\text{Pt–C})$ 1586.2 Hz, compared with 1564.6 Hz for the *trans* isomer in $\text{SOCl}_2/\text{CD}_2\text{Cl}_2$; *cis*- $\text{PtI}_2(\text{CO})_2$ has $J(\text{Pt–C})$ 1521 in benzene, compared with 1469.7 Hz for *trans*- $\text{PtI}_2(\text{CO})_2$ in the same solvent). In the tertiary phosphine series, on the other hand, *cis*- $\text{PtCl}_2(\text{PPh}_3)_2$ has $J(\text{Pt–P})$ 3508 Hz and the *trans* isomer has $J(\text{Pt–P})$ 2380 Hz in the same solvent (CHCl_3). In other words, it appears that, within the validity of the approximations used, the Pt–CO bond strength is about the same for both the *cis* and the *trans* geometries. Chemical support for this suggestion comes from the behaviour of $\text{PtI}_2(\text{CO})_2$ in solvents of low polarity, in which the two isomers do not greatly differ in energy, as shown by the fact that the *cis* and *trans* species coexist (see eq. 16). If the isomer ratio is *trans*/*cis* = 95/5, this would correspond to an equilibrium constant of about 20, for a ΔG° of about 2 kcal mol⁻¹. When dealing with such small energies, any interpretation of the data can only be qualitative.

A common feature for tertiary-phosphine and carbonyl complexes of platinum(II) is that the dimeric species $\text{Pt}_2\text{X}_4\text{L}_2$ (L = PR_3 , CO) show the highest $J(\text{Pt–Y})$

values. By including for the carbonyl complexes the NMR data reported for the anionic $[\text{PtX}_2(\text{CO})]^-$ complexes (see Table 4), it can be seen that the $J(\text{Pt}-\text{C})$ decrease in the sequence shown below. The main factor influencing the value of the



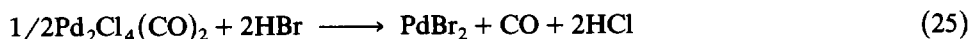
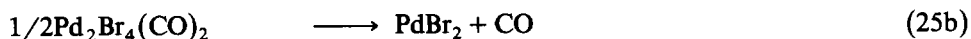
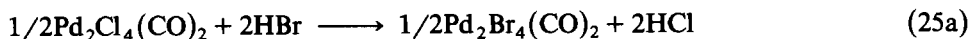
coupling constant is the number of halide ligands *per* platinum: it is therefore to be expected that the more electronegative the halide the stronger the σ -component within the Pt-CO bond.

As in the previously studied case of the tertiary phosphine complexes [55], an important position is occupied by the platinum(IV) complexes, namely $[\text{PtCl}_5(\text{CO})]^-$ and $[\text{PtBr}_5(\text{CO})]^-$. These compounds, which are prepared by chlorine [59,21c] or bromine [59] oxidation of the corresponding $[\text{PtX}_3(\text{CO})]^-$ complexes, are characterized by values of $J(\text{Pt}-\text{C})$ around 1200 Hz, i.e. lower than for any of the platinum(II) complexes. This is understandable, since the central metal atom uses d^2sp^3 hybridization, the s contribution to the Pt-C bond therefore being smaller. Moreover, the data for the platinum(IV) complexes allow some general conclusions to be drawn about the nature of the Pt-CO bond. When it is noted [21c] that $[\text{PtCl}_5(\text{CO})]^-$ has an extremely high $\tilde{\nu}(\text{CO})$ (2191 cm^{-1} in thionyl chloride), and that we are dealing with a relatively high oxidation state of the metal, an appreciable π -back bonding contribution can be excluded. However, the trend in $J(\text{Pt}-\text{C})$ on going from the chloride to the bromide is the same ($\text{Cl} > \text{Br}$) as that observed for the series of the platinum(II) complexes. This suggests that arguments based on predominant σ -contributions to the bonding should be able to explain the observed facts.

The bromo carbonyl complexes of palladium(II) and gold(I)

In view of the presumably lower M-CO bond energy in the $\text{Cl} > \text{Br}$ sequence, which is probably paralleled by a decrease in the M-X bond energy in the same sequence, isolation of the bromo carbonyl derivatives of palladium(II) and gold(I) presented a challenging problem. After several attempts, isolation of $\text{Pd}_2\text{Br}_4(\text{CO})_2$, though always contaminated by PdBr_2 [60] was achieved by operating at elevated pressures of carbon monoxide in toluene as solvent, according to the stoichiometry of eq. 24. The solution containing the carbonyl derivative showed an IR band at 2148 cm^{-1} , attributed to the carbonyl stretching vibration of the dimeric bromo carbonyl, with a presumably centrosymmetric structure of C_{2h} symmetry. This frequency should be compared with that of 2119 cm^{-1} (see Table 2) observed for the corresponding platinum(II) species, $\text{Pt}_2\text{Br}_4(\text{CO})_2$. It is therefore once more confirmed that the $\tilde{\nu}(\text{CO})$ decreases systematically in the sequence $\text{Pd} > \text{Pt}$, for compounds of similar molecular structure and, of course, with the same oxidation state of the central metal. Quenching at dry-ice temperature of the solution resulting from the carbonylation reaction of eq. 24 allowed isolation of $\text{Pd}_2\text{Br}_4(\text{CO})_2$ as an orange solid, rapidly darkening at room temperature due to loss of coordinated CO. These findings suggest that the bromo carbonyl is observable only under a relatively high CO pressure, in accord with equilibrium 24. Evidence for the transient formation of $\text{Pd}_2\text{Br}_4(\text{CO})_2$ at atmospheric pressure of CO or lower comes from the attempted preparation of $\text{Pd}_2\text{Br}_4(\text{CO})_2$ by the exchange reaction with HBr (25a). The actual result of the attempted halide exchange was the formation of PdBr_2 .

However, no halide exchange was found to occur in the PdCl_2/HBr system unless carbon monoxide was present.



The bromo carbonyl of gold(I), $\text{AuBr}(\text{CO})$ can be prepared in a halogenated solvent starting from either Au_2Br_6 or AuBr [24]. In the former case the presence of a bromine acceptor, such as carbon monoxide or cyclohexene, is required. However, carbon monoxide does not act as an efficient halogen acceptor, in contrast to the case shown in eq. 7, because of the less favourable thermodynamic situation for COBr_2 [61] (see eq. 26) than for COCl_2 [43] (see eq. 3). Although about $10^{-2} M$



solutions of $\text{AuBr}(\text{CO})$, characterized spectroscopically [$\tilde{\nu}(\text{CO}) = 2153 \text{ cm}^{-1}$ in *sym*-dibromoethane, ^{13}C NMR (at -70°C), δ , 173.8 ppm from TMS in CD_2Cl_2] can be prepared, attempts to isolate the solid product failed due to its rapid decomposition with loss of bound carbon monoxide.

Conclusions

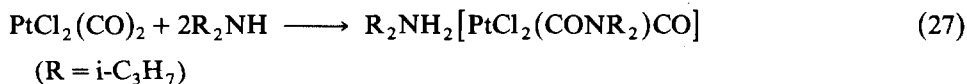
The studies carried out up to now on the halo carbonyls of palladium, platinum and gold appear to confirm the validity of the earlier suggestion [8] by Malatesta and Naldini that the stability of halo carbonyls of platinum(II) decrease in the sequence $\text{Cl} > \text{Br} > \text{I}$, and show that the sequence can be extended to the palladium and gold derivatives. This is particularly evident in the case of the bromo derivatives of palladium(II) and gold(I), which undergo a fast decomposition to the corresponding metal bromides to some extent. Solutions of the bromo carbonyls in halogenated solvents are stable only under carbon monoxide, at elevated (Pd) or atmospheric (Au) pressure. This behaviour contrasts with the relative stability of $\text{Pd}_2\text{Cl}_4(\text{CO})_2$ and the indefinite stability of $\text{AuCl}(\text{CO})$.

The observed trend of stability in the sequence $\text{Cl} > \text{Br} > \text{I}$ may be due to decrease in the $\text{M}-\text{CO}$ bond strength in the same sequence or to decrease in the $\text{M}-\text{X}$ bond strength or to both. The last suggestion is preferred, i.e. it is probable that both $\text{M}-\text{CO}$ and $\text{M}-\text{X}$ bonds become weaker along the sequence $\text{Cl} > \text{Br} > \text{I}$, although no well established quantitative data are available to verify this hypothesis. The values of $J(\text{Pt}-\text{C})$ decrease in the sequence $\text{Cl} > \text{Br} > \text{I}$, suggesting a fall of the σ -bond strength within the $\text{Pt}-\text{CO}$ system in the same sequence. Since a decrease in the value of $J(\text{Pt}-\text{C})$ is also observed for the halo carbonyl derivatives of platinum(IV), $[\text{PtX}_5(\text{CO})]^-$, for which no question of π -back-bonding arises, it follows that the observed trend of $J(\text{Pt}-\text{C})$ as a function of the bonded halide must be accounted for outside the framework of the π -back-bond formulation. The values of $\tilde{\nu}(\text{CO})$ also decrease in the sequence $\text{Cl} > \text{Br} > \text{I}$. If the σ -component predominant, the increase of $\tilde{\nu}(\text{CO})$ in the sequence $\text{I} < \text{Br} < \text{Cl}$ may be due to a progressively larger transfer of electron density to the metal from the lone pair on the

carbonyl carbon, the 5σ orbital, which has a slight antibonding character [62]. It has been pointed out that removal of one electron from the 5σ orbital to give CO^+ reduces the internuclear distance from 1.128 to 1.115 Å, while the value of $\bar{\nu}(\text{CO})$ increases [63] slightly from 2143 to 2184 cm^{-1} .

If the σ component of the M–CO bond for these late transition elements is predominant, several experimental observations can be accounted for. In the absence of any important π -back component, the overall strength of the bond would not increase by lowering the oxidation state of the metal. Thus, if, for example, the value of about 24 kcal mol^{-1} estimated for the Pd^{II} –CO bond would not be increased by reducing the oxidation state of palladium, or if the value could possibly become lower this provides an explanation of the unavailability of $\text{Pd}(\text{CO})_4$ from the element and its decomposition to its components [5].

A quite large polarity of the M–CO bond would be expected in terms of the assumption of a predominant σ -contribution. The reaction of $\text{PtCl}_2(\text{CO})_2$ with secondary amines [64] to give the corresponding carbamoyl derivatives (see eq. 27) is consistent with this view. Reaction 27 is fast and is reversible, i.e. treatment of the carbamoyl derivative with hydrogen chloride regenerates $\text{PtCl}_2(\text{CO})_2$.



The basic information gathered for the M–CO bond in these systems can probably be carried over to systems containing the M–olefin bond. It is noteworthy, in this connection, that Zeise's salt $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$ has been recently reinvestigated [65] spectroscopically, and data interpreted in terms of a predominant σ -component in the platinum–olefin bond.

Acknowledgements

The author is indebted to all his coworkers, whose names are in the list of references. Financial support from the Consiglio Nazionale delle Ricerche (C.N.R., Roma), Progetto Finalizzato di Chimica Fine II, is gratefully acknowledged.

References

- 1 P. Schützenberger, *Annales (Paris)*, 15 (1868) 100; *Bull. Soc. Chim. France*, 14 (1870) 97.
- 2 M. Herberhold, *Metal π -Complexes*, Vol. 2, Elsevier, Amsterdam, 1974, and references therein.
- 3 L. Mond, C. Langer and F. Quincke, *J. Chem. Soc. (London)*, 57 (1890) 749.
- 4 E. Abel, *J. Organomet. Chem.*, 383 (1990) 11.
- 5 H. Huber, P. Kündig, M. Moskovits and G.A. Ozin, *Nature (London)*, 235 (1972) 98; J.H. Darling and J.S. Ogden, *Inorg. Chem.*, 11 (1972) 666; E.P. Kündig, D. McIntosh, M. Moskovits and G.A. Ozin, *J. Am. Chem. Soc.*, 95 (1973) 7234.
- 6 W.E. Dasent, *Nonexistent compounds*, M. Dekker, New York, 1965, p. 8.
- 7 F. Mylius and F. Foerster, *Chem. Ber.*, 24 (1891) 2424.
- 8 L. Malatesta and L. Naldini, *Gazz. Chim. Ital.*, 90 (1960) 1505.
- 9 P.L. Goggin, R.J. Goodfellow, I.R. Herbert and A.G. Orpen, *J. Chem. Soc., Chem. Commun.*, (1981) 1077.
- 10 P.L. Goggin and J. Mink, *J. Chem. Soc., Dalton Trans.*, (1974) 534.
- 11 W. Manchot and H. Gall, *Chem. Ber.*, 58 (1925) 2175.
- 12 D. Belli Dell'Amico and F. Calderazzo, *Gazz. Chim. Ital.*, 103 (1973) 1099.
- 13 G. Brauer, *Handbook of preparative inorganic chemistry*, Vol. 2, Academic Press, New York, 1965, p. 1056.

- 14 N.B. North, *Bull. Soc. Chim. France*, 9 (1910) 646; *Chem. Zentralbl.*, 82 II (1911) 665.
- 15 V. Gutmann, *Z. Anorg. Allg. Chem.*, 264 (1951) 169.
- 16 M.E. Diemer, *J. Am. Chem. Soc.*, 35 (1913) 553.
- 17 H. Funk and H. Köhler, *Z. Anorg. Allg. Chem.*, 294 (1958) 233.
- 18 D. Belli Dell'Amico and F. Calderazzo, *Inorg. Synth.*, 24 (1984) 236.
- 19 M.S. Kharasch and H.S. Isbell, *J. Am. Chem. Soc.*, 52 (1930) 2919.
- 20 D. Belli Dell'Amico and A. Morvillo, unpublished results.
- 21 (a) D. Belli Dell'Amico, F. Calderazzo and F. Marchetti, *J. Chem. Soc., Dalton Trans.*, (1976) 1829; (b) D. Belli Dell'Amico, F. Calderazzo, F. Marchetti, S. Merlino and G. Perego, *Chem. Commun.*, (1977) 31; (c) D. Belli Dell'Amico, F. Calderazzo, F. Marchetti and S. Merlino, *J. Chem. Soc., Dalton Trans.*, (1982) 2257.
- 22 W.B. Pearson, *Lattice Spacings and Structures of Metals and Alloys*, Pergamon Press, London, 1957.
- 23 P.G. Jones, *Gold Bull.*, 14 (1981) 102; *idem, ibid.*, 14 (1981) 159.
- 24 (a) P. Robino, Thesis, University of Pisa, 1989; (b) D. Belli Dell'Amico, F. Calderazzo, P. Robino and A. Segre, *Gozz. Chim. Ital.*, submitted.
- 25 F. Basolo and R.G. Pearson, *Mechanisms of inorganic reactions*, 2nd ed., J. Wiley, New York, 1968.
- 26 D. Belli Dell'Amico, F. Calderazzo and G. Dell'Amico, *Gazz. Chim. Ital.*, 107 (1977) 101.
- 27 D. Belli Dell'Amico and F. Calderazzo, *Gazz. Chim. Ital.*, 109 (1979) 99.
- 28 B.P. Andreini, D. Belli Dell'Amico, F. Calderazzo, M.G. Venturi, G. Pelizzi and A. Segre, *J. Organomet. Chem.*, 354 (1988) 357.
- 29 L. Romberg, *Z. Anorg. Allg. Chem.*, 83 (1913) 36.
- 30 N. Pasqualetti, Thesis, University of Pisa, 1988.
- 31 J. Browning, P.L. Goggin, R.J. Goodfellow, M.G. Norton, A.J.M. Rattray, B.F. Taylor and J. Mink, *J. Chem. Soc., Dalton Trans.*, (1977) 2061.
- 32 D.R. Stull, E.F. Westrum and G.C. Sinke, *The chemical thermodynamics of organic compounds*, J. Wiley, New York, 1969.
- 33 B.P. Andreini, D. Belli Dell'Amico, F. Calderazzo and N. Pasqualetti, *Inorg. Synth.*, submitted.
- 34 R.D. Rogers, H. Isci and W.R. Mason, *J. Cryst. Spectrosc. Res.*, 14 (1984) 383.
- 35 M.R. Churchill and S.A. Julis, *Inorg. Chem.*, 18 (1979) 1215.
- 36 C.D. Cowman, J.C. Thibeault, R.F. Ziolo and H.B. Gray, *J. Am. Chem. Soc.*, 98 (1976) 3209.
- 37 (a) N.C. Stephenson, *Acta Cryst.*, 17 (1964) 587; (b) D.R. Russell, P.A. Tucker and C. Whittaker, *Acta Crystallogr.*, B31 (1975) 2530.
- 38 E.M.W. Janssen, J.C.W. Folmer and G.A. Wieggers, *J. Less-Common Metals*, 38 (1974) 71.
- 39 P.G. Jones, *Z. Naturforsch. B*, 37 (1982) 823.
- 40 (a) W.E. Bell, U. Merten and A. Tagami, *J. Phys. Chem.*, 65 (1961) 510; (b) H. Schäfer, U. Wiese, K. Rinke and K. Brendel, *Angew. Chem.*, 79 (1967) 244.
- 41 H. Schäfer and H.G. Schnering, *Angew. Chem.*, 76 (1964) 833.
- 42 (a) F. Calderazzo and F.A. Cotton, *Inorg. Chem.*, 1 (1962) 30; (b) F. Calderazzo, G. Fachinetti and C. Floriani, *J. Am. Chem. Soc.*, 96 (1974) 3695.
- 43 *CRC Handbook of Chemistry and Physics*, 65th ed., CRC Press, Boca Raton, Florida, 1985.
- 44 J.A. Connor, *Topics Curr. Chem.*, 71 (1977) 71.
- 45 D. Belli Dell'Amico, F. Calderazzo, C.A. Veracini and N. Zandonà, *Inorg. Chem.*, 23 (1984) 303; *idem, ibid.*, 23 (1984) 4871.
- 46 G. Thiele and D. Wagner, *Chem. Ber.*, 111 (1978) 3162.
- 47 W. Manchot and J. König, *Chem. Ber.*, 59 (1926) 883.
- 48 R. Colton, R.H. Farthing and M.J. McCormick, *Aust. J. Chem.*, 26 (1973) 2607.
- 49 R.J. Irving and E.A. Magnusson, *J. Chem. Soc.*, (1958) 2283, and references therein.
- 50 P.M. Maitlis, *The organic chemistry of palladium*, Vol. 2, Academic Press, New York, 1971.
- 51 (a) F. Calderazzo and D. Belli Dell'Amico, *Inorg. Chem.*, 20 (1981) 1310; (b) D. Belli Dell'Amico, F. Calderazzo and N. Zandonà, *ibid.*, 23 (1984) 137.
- 52 R. Usò, J. Forniés, M. Tomàs and B. Menjòn, *Organometallics*, 4 (1985) 1912.
- 53 H. Babad and A.G. Zeiler, *Chem. Rev.*, 72 (1973) 75.
- 54 W.J. Cherwinski, B.F.G. Johnson, J. Lewis and J.R. Norton, *J. Chem. Soc., Dalton Trans.*, (1975) 1156.
- 55 A. Pidcock, R.E. Richards and L.M. Venanzi, *J. Chem. Soc., A*, (1966) 1707.
- 56 C.D. Cook and K.Y. Wan, *J. Am. Chem. Soc.*, 92 (1970) 2595.
- 57 J.B. Stothers, *Carbon-13 NMR spectroscopy*, A series of monographs in Organic Chemistry, Vol. 24, Academic Press, New York, 1972.

- 58 H.A. Skinner, *Adv. Organomet. Chem.*, 2 (1964) 49.
- 59 C. Crocker, P.L. Goggin and R.J. Goodfellow, *J. Chem. Soc., Chem. Commun.*, (1978) 1056.
- 60 B.P. Andreini, D. Belli Dell'Amico, F. Calderazzo, M.G. Venturi and G. Pelizzi, *J. Organomet. Chem.*, 354 (1988) 369.
- 61 H.J. Schumacher and S. Lehner, *Chem. Ber.*, 61 (1928) 1671.
- 62 R.S. Mulliken and W.C. Ermler, *Diatomic molecules*, Academic Press, New York, 1977.
- 63 J.B. Johnson and W.G. Klemperer, *J. Am. Chem. Soc.*, 99 (1977) 7132.
- 64 D. Belli Dell'Amico, F. Calderazzo and G. Pelizzi, *Inorg. Chem.*, 18 (1979) 1165.
- 65 T.H. Chang and J.I. Zink, *J. Am. Chem. Soc.*, 106 (1984) 287.