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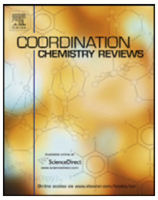

Review

Halo-carbonyl complexes of palladium, platinum and gold

Daniela Belli Dell'Amico*, Luca Labella, Fabio Marchetti, Simona Samaritani

Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via Risorgimento 35, 56126 Pisa, Italy

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ABSTRACT

In this review we summarize some recent literature data concerning synthetic procedures, properties, structure, reactivity and applications of halo-carbonyl complexes of palladium, platinum and gold, taking into consideration that the organometallic chemistry of these metals, with a particular attention to the halo-carbonyls, has been reviewed 20 years ago [F. Calderazzo, J. Organomet. Chem. 400 (1990) 303]. A brief overview of the early studies is provided.

1. Introduction

Chloro-carbonyl complexes of platinum and gold are milestones in the organometallic chemistry of transition metals. Among the metal carbonyls $[PtCl_2(CO)_2]$ and $[Pt_2Cl_4(CO)_2]$ were prepared by Schützenberger [2], 22 years before the well celebrated nickel tetracarbonyl, obtained by Mond et al. [1] by reaction of platinum sponge with Cl_2 and CO at high temperature [2]. The gold(I) species [AuCl(CO)] was prepared by Manchot and Gall [3] and later on by Kharasch and Isbell [4] by carbonylation of gold chlorides (AuCl, Au_2Cl_6) through dry and/or wet methods. The palladium(II) chloro-carbonyl $[Pd_2Cl_4(CO)_2]$ was conveniently obtained by reacting $PdCl_2$ and CO in thionyl chloride as solvent [5]. Earlier reports about a species proposed as $[PdCl_2(CO)]$ are in contrast with the reactivity of the palladium(II) derivative toward the solvent used in the preparation (methanol) [6] or with the reported CO stretching wave-number value ($\tilde{\nu}_{CO} = 1947\,cm^{-1}$) [7]. The chloro-carbonyls [*cis*-$PtCl_2(CO)_2$], $[Pt_2Cl_4(CO)_2]$, $[Pd_2Cl_4(CO)_2]$ and [AuCl(CO)] are all characterized by $\tilde{\nu}_{CO}$ values which are close to or higher than that of free CO ($2143\,cm^{-1}$).

In the model of synergistic CO-to-metal σ-donation and metal-to-CO π-back-donation, $\tilde{\nu}_{CO}$ values are often used as a probe of the nature of the metal–CO bond in metal carbonyls, a value higher than $2143\,cm^{-1}$ being considered the clue of a minimal contribution of π-back-donation. In a carbonyl complex the metal centre can be little inclined to π-back-donation for different reasons: for instance for lack of d electrons, or for the relatively low energy of the d electrons with respect to the antibonding CO orbitals. The latter reason is expected to be relevant for late transition metals of the second and third series, characterized by a relatively high electronegativity [8].

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* Corresponding author. Tel.: +39 050 2219210; fax: +39 050 2219260.
E-mail address: belli@dcci.unipi.it (D.B. Dell'Amico).

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In complexes where the metal–CO bond is based essentially on the σ-component, we can expect that its strength increases with the positive charge density on the metal centre. It is interesting to note that several carbonyls of palladium, platinum and gold are known where these elements have an oxidation number higher than zero. Among them even salts containing binary cationic carbonyls, like $[M(CO)_4]^{2+}$, have been isolated in the last decades [9]. On the contrary, molecular neutral binary carbonyls were never obtained, aside from condensation in matrix at low temperature starting from metal atoms and CO [10,11]. This behaviour agrees with a metal–CO bond being essentially sigma in nature. Also the relative stability of the halo-carbonyl complexes, which decreases in the sequence chloride > bromide > iodide is in agreement with such an interpretation of the nature of the M–CO bond [12]. Moreover, the reactivity of these carbonyls, that easily undergo attack by nucleophiles to the carbon atom of the coordinated CO [13], is consistent with this description. For these reasons, some years ago, the halo-carbonyls of palladium(II), platinum(II) and gold(I) were named "atypical" [14].

In the last 17 years excellent results have been obtained concerning the synthesis and characterization of a series of metal carbonyls where the metal–CO bond was considered to be essentially σ in nature [9,15] and the names σ-carbonyls [9b] or nonclassical [15a] metal carbonyls have been proposed [15a]. The $\tilde{\nu}_{CO}$ values alone are not sufficient to exclude the contribution of π-back-bonding to the M–CO bond [16]. Nevertheless, these spectroscopic data are easily obtainable, and can correctly advise about the nature of the M–CO bond.

Theoretical contributions concerning the electronic structure of CO [17] and the nature of the M–CO bond [18], correlated with the physical properties of transition metals carbonyls, have appeared. To consider C–O stretching frequencies as evidence of a prevalence of σ-donation or π-back-donation is "dangerous [18], because the conclusion from theoretical work suggests that electrostatic interactions are important as orbital interaction for the binding energies" and "may play a role for the C–O stretching frequencies". According to some calculations high C–O stretching frequencies in metal carbonyls appear to be caused only by electrostatic effects and not by σ-donation [18b]. A recent paper proposes the use of the relationships linking ^{13}C and ^{18}O isotopic effects on the C–O stretching vibrations to the force constant of the M–CO coordination bond [19].

Experimental data concerning the M–CO bond dissociation energies (BDE) in the complexes which are the subject of this review are rare. The value of about 100 kJ mol^{-1} for the Pd–CO BDE in $[Pd_2Cl_4(CO)_2]$ was obtained by the study of the equilibrium reaction (1) carried out in $SOCl_2$ [20].

$$2PdCl_{2(s)} + 2CO \rightleftharpoons [Pd_2Cl_4(CO)_2] \tag{1}$$

The Pt–CO bond is expected to be stronger, as usually observed moving in a group of the d block from the second to the third transition series, according to both experimental and theoretical data [21]. Recent data which allow a comparison between iridium and rhodium concerning the bond of CO with the fragments $[MCl(P^iPr_3)_2]$ (M = Rh, Ir) have been reported: the lower limits for the M–CO BDE have been estimated to be 202 [22] and 294 kJ mol^{-1} [23], respectively.

Calculated values of the Au–CO BDE in [AuCl(CO)] [24] agree with that estimated on the base of thermodynamic data, corresponding to about 200 kJ mol^{-1} [25].

In the last two decades some new studies on the simple derivatives $[MX_n(CO)_m]_x$ X = Cl, Br, I; M = Pd, Pt, Au and related species have been carried out, especially concerning their preparation, structure and reactivity. Herein we present a discussion of the results obtained in our laboratories and elsewhere.

2. Preparations and properties

Attempts to prepare the unknown [AuBr(CO)] and [AuI(CO)] of Au_2Br_6 produces an equilibrium mixture according to Eq. (2a).

$$Au_2Br_6 + 4CO \rightleftharpoons 2[AuBr(CO)] + 2COBr_2 \tag{2a}$$

$$CO + Br_2 \rightleftharpoons COBr_2 \tag{2b}$$

Because of the thermodynamic instability of $COBr_2$ with respect to CO + Br_2 (see Eq. (2b), ΔG° = +26.3 kJ mol^{-1} [26]), a stoichiometric amount of an alkene (for instance cyclohexene, C_6H_{10}), able to scavenge Br_2, was added to the system to favour the production of [AuBr(CO)]. An alternative path is the reaction of AuBr with CO (see Eq. (3)), AuBr being easily prepared by reduction of Au_2Br_6 with the stoichiometric amount of an alkene (see Eq. (4)).

$$AuBr + CO \rightarrow [AuBr(CO)] \tag{3}$$

$$Au_2Br_6 + 2C_6H_{10} \rightarrow 2AuBr + 2C_6H_{10}Br_2 \tag{4}$$

Although the bromo-carbonyl of gold is stable in solution under CO, as observed in a quantitative control of the CO uptake by AuBr (P_{CO} = 1 atm, T = 17 °C, in CH_2Br_2 as solvent), attempts to isolate the solid product failed, probably for its low stability under reduced pressure of CO. IR and ^{13}C NMR characterization of the product in solution was carried out and the data here are compared with those of [AuCl(CO)]: $\tilde{\nu}_{CO}$ (cm^{-1}) 2162 and 2159 (solvent CH_2Cl_2) for [AuCl(CO)] and [AuBr(CO)], respectively; δ from TMS 172.3 and 174.4 ppm (T = 0 °C; solvent CD_2Cl_2) for [AuCl(CO)] and [AuBr(CO)], respectively.

Attempted syntheses of [AuI(CO)] were unsuccessful. AuI, as obtained by reaction of Au_2Cl_6 with ^{i}PrI, decomposes under CO with formation of metallic gold and I_2. The addition of ^{i}PrI to [AuCl(CO)], produces metallic gold and I_2, presumably through an unstable [AuI(CO)] as intermediate [12c,d].

The stability trend observed for the [AuX(CO)] derivatives (X = Cl, Br, I) confirms the low degree of metal-to-CO π retrodonation in the Au–CO bond, as already discussed in Section 1.

[AuX(CO)] (X = F, Cl, Br) [27] and more recently [AuI(CO)] [28] were generated in the gas phase by reacting gold vapour with CO and a halide precursor. High resolution microwave spectroscopic measurements allowed the determination of the ground state molecular geometry. The molecules are linear, with Au–CO bond distances of 184.7, 188.4, 189.2 and 190.8 pm for X = F, Cl, Br and I, respectively. This trend suggests a decrease in the bond strength in the series. The Au–CO bond distance is 193 pm in solid [AuCl(CO)] [29], where Au···Au and C···Cl intermolecular interactions are not negligible.

A theoretical study concerning the relative stability of the complexes [MCl(CO)], M being a group 11 metal, has been carried out at the *ab initio* level using relativistic and non-relativistic energy adjusted pseudopotentials for the metal atoms [24a]. [AuCl(CO)] is relativistically stabilized, the calculated Au–CO BDE being 182 kJ mol^{-1}. According to the authors, both σ and π contributions to the bond appear to be important.

A different conclusion was obtained in the course of a study concerning gaseous $[Au(CO)_n]^+$ ions, generated with a laser vapourization source, analysed by IR photodissociation spectroscopy. From associated theoretical studies [30], the authors conclude that σ donation from CO to the metal ion describes the bonding in these systems, while back-donation is considered inefficient.

Gold carbonyl complexes where the metal shows an oxidation number higher than +I are not characterized. Nevertheless, papers dealing with CO coordinated to gold ions supported on Zeolite NaY have been published [31] and the authors assign IR bands observed at 2207 and in the region 2171–2186 cm^{-1} to cationic gold(III) carbonyls. They support their hypothesis with further experimental data, being aware that the CO stretching frequency alone is not sufficient to assign the gold oxidation number. In fact, several Au(I) carbonyl complexes show a rather high CO stretching frequency: $[Au(CO)_2][Y]$ ($Y = SO_3F$ [32], Sb_2F_{11} [33], UF_6 [34]), containing the $[Au(CO)_2]^+$ cation and the species $[Au(CO)(SO_3F)]$ [32] absorb at 2211, 2217, 2200 and 2195 cm^{-1}, respectively. Moreover, the mixed-valence carbonyl $[Au_2Cl_4(CO)]$ [12d,35], which is considered a dinuclear complex containing a planar $AuCl_4$ unit connected via a chloride bridge to the AuCO moiety, is characterized by a CO stretching at 2180 cm^{-1}. The last species, spectroscopically detected in the course of the reductive carbonylation of Au_2Cl_6, has been subsequently isolated as the product of the reaction of Au_2Cl_6 with $[AuCl(CO)]$ (in 1:2 molar ratio) carried out at −33 °C [12d] (Eq. (5)).

$$Au_2Cl_6 + 2[AuCl(CO)] \rightarrow 2[Au_2Cl_4(CO)] \quad (5)$$

Its ^{13}C NMR spectrum recorded at −50 °C in CD_2Cl_2 shows a single signal at 170.8 ppm from TMS, to be compared with the signal at 171.8 ppm observed for $[AuCl(CO)]$ in the same conditions. At room temperature in solution the product decomposes to AuCl and $COCl_2$ (Eq. (6)).

$$[Au_2Cl_4(CO)] \rightarrow 2AuCl + COCl_2 \quad (6)$$

Carbonyl complexes of metals with oxidation number +IV are rare: they are encountered for early transition metals in the presence of the ligands Cp ($[C_5H_5]^-$) or Cp* ($[C_5Me_5]^-$) [36], while for late transition metals, to the best of our knowledge, only platinum derivatives are known. Among the rare halo-carbonyl complexes of platinum(IV), salts containing the anion $[PtCl_5(CO)]^-$ have been isolated ($\tilde{\nu}_{CO}$ 2191 cm^{-1} for $[NH_2{}^iPr_2][PtCl_5(CO)]$) [37]. Recently, the species $[NBu_4][trans\text{-}PtBr(C_6F_5)_4(CO)]$ ($\tilde{\nu}_{CO}$ 2166 cm^{-1}) has been obtained by oxidative addition of Br_2 to $[NBu_4]_2[Pt(C_6F_5)_4]$, followed by partial halide extraction with $AgClO_4$ under CO [38]. Its molecular and crystal structures have been determined (see Section 3).

Concerning oxidation number +II, new preparative routes to $[PtCl_2(CO)_2]$ have been reported [39]. The carbonylation of $[NBu_4]_2[PtCl_4]$ in CH_2Cl_2, assisted by $AlCl_3$, affords $[trans\text{-}PtCl_2(CO)_2]$ [40], which easily isomerizes to the *cis*-complex (see Eqs. (7)–(9)). It is convenient to carry out the reaction in two steps, represented by Eqs. (7) and (8), to avoid precipitation of $PtCl_2$, which reacts rather slowly with CO.

$$[PtCl_4]^{2-} + AlCl_3 + CO \rightarrow [PtCl_3(CO)]^- + [AlCl_4]^- \quad (7)$$

$$[PtCl_3(CO)]^- + AlCl_3 + CO \rightarrow [trans\text{-}PtCl_2(CO)_2] + [AlCl_4]^- \quad (8)$$

$$[trans\text{-}PtCl_2(CO)_2] \rightleftharpoons [cis\text{-}PtCl_2(CO)_2] \quad (9)$$

The intermediate formation of the kinetic product of reaction 8, $[trans\text{-}PtCl_2(CO)_2]$, is observed by IR spectroscopy.

A second route to $[cis\text{-}PtCl_2(CO)_2]$ is the reaction of SO_2Cl_2 with $[PtI_2(CO)_2]$, easily obtained by carbonylation of PtI_2 in mild conditions (Eq. (10)).

$$[PtI_2(CO)_2] + SO_2Cl_2 \rightarrow [cis\text{-}PtCl_2(CO)_2] + I_2 + SO_2 \quad (10)$$

A further preparation is the reaction of $[Pt(CO)_2]_n$ (obtained by contacting platinum(0) olefin complexes with CO) with SO_2Cl_2 under CO (see reaction (11a)) [41a].

$$1/n[Pt(CO)_2]_n + SO_2Cl_2 \rightarrow [cis\text{-}PtCl_2(CO)_2] + SO_2 \quad (11a)$$

Connected with this reaction is the oxidation of $[Pt(CO)_2]_n$ by I_2 under CO which affords $[PtI_2(CO)_2]$ (see reaction (11b)) [41b].

$$1/n[Pt(CO)_2]_n + I_2 \rightarrow [PtI_2(CO)_2] \quad (11b)$$

Under the same conditions $[Pd_2(CO)_y]_n$ ($y \sim 1$), obtained by $[Pd(dba)_2]$ (dba = dibenzylideneacetone) and CO at room temperature produces $[Pd_2Cl_4(CO)_2]$ (Eq. (12)).

$$1/n[Pd_2(CO)_y]_n + CO + 2SO_2Cl_2 \rightarrow [Pd_2Cl_4(CO)_2] + 2SO_2 \quad (12)$$

Also platinum and palladium blacks, although more slowly, react with SO_2Cl_2 under CO at room temperature affording $[cis\text{-}PtCl_2(CO)_2]$ and $[Pd_2Cl_4(CO)_2]$, respectively [41].

$$Pt + SO_2Cl_2 + 2CO \rightarrow [cis\text{-}PtCl_2(CO)_2] + SO_2 \quad (13a)$$

$$2Pd + 2SO_2Cl_2 + 2CO \rightarrow [Pd_2Cl_4(CO)_2] + 2SO_2 \quad (13b)$$

In the absence of CO no attack to the metal by SO_2Cl_2 is observed.

A convenient preparation of the dinuclear platinum complex $[Pt_2Cl_4(CO)_2]$ has been described. It can be obtained by reaction (7) followed by addition of a second equivalent of $AlCl_3$ carried out under N_2 (Eq (14)) [39b].

$$2[PtCl_3(CO)]^- + 2AlCl_3 \rightarrow [Pt_2Cl_4(CO)_2] + 2[AlCl_4]^- \quad (14)$$

This dinuclear platinum complex promptly reacts with CO, so care must be used to avoid the presence of free CO in the second step of its synthesis. The analogous palladium dimer $[Pd_2Cl_4(CO)_2]$ does not react further with CO and can be prepared in one step according to Eq. (15) [39b].

$$2[PdCl_4]^{2-} + 4AlCl_3 + 2CO \rightarrow [Pd_2Cl_4(CO)_2] + 4[AlCl_4]^- \quad (15)$$

$[Pd_2Cl_4(CO)_2]$ is in equilibrium with $PdCl_2$ and CO [20] and the reaction can be exploited to prepare the β-phase of the palladium dichloride. Single crystals of Pd_6Cl_{12} can be grown by slowly decreasing the partial pressure of CO on a solution of the chloro-carbonyl complex (see Eq. (16)) [42].

$$3[Pd_2Cl_4(CO)_2] \rightleftharpoons Pd_6Cl_{12} + 6CO \quad (16)$$

Concerning bromo-carbonyl complexes of platinum(II) the synthesis of $[cis\text{-}PtBr_2(CO)_2]$ by extraction of bromide ions from $[PtBr_4]^{2-}$ with $AlBr_3$ in the presence of CO (Eqs. (17)–(19)) follows the path already seen for the chloro-derivative (Eqs. (7)–(9)), with the intermediate formation of $[trans\text{-}PtBr_2(CO)_2]$, characterized by a CO stretching vibration at 2142 cm^{-1} in dichloroethane [39b].

$$[PtBr_4]^{2-} + AlBr_3 + CO \rightarrow [PtBr_3(CO)]^- + [AlBr_4]^- \quad (17)$$

$$[PtBr_3(CO)]^- + AlBr_3 + CO \rightarrow [trans\text{-}PtBr_2(CO)_2] + [AlBr_4]^- \quad (18)$$

$$[trans\text{-}PtBr_2(CO)_2] \rightleftharpoons [cis\text{-}PtBr_2(CO)_2] \quad (19)$$

An alternative synthesis is represented by the reaction of $[cis\text{-}PtCl_2(CO)_2]$ with a moderate excess of ^iPrBr (Eq. (20)), the formation of the strong C–Cl bond being the driving force of the process [39b,43].

$$[cis\text{-}PtCl_2(CO)_2] + 2{}^iPrBr \rightarrow [cis\text{-}PtBr_2(CO)_2] + 2{}^iPrCl \quad (20)$$

Although PtI_2 reacts rapidly with CO (RT, $P_{CO} = 1$ atm) with formation of an equilibrium mixture of *cis*- and $[trans\text{-}PtI_2(CO)_2]$ (the *trans*-isomer being prevalent) [12a], $PtCl_2$ and $PtBr_2$ react rather slowly in the same conditions, and higher temperatures are recommended for preparative aims.

As discussed in Section 1, the stability of the halo-carbonyl derivatives of Pd(II), Pt(II) and Au(I) diminishes with the increase of the atomic number of the halide [12]. Therefore we can expect that the fluoro-carbonyls are the most stable derivatives of the family. Nevertheless, metal fluoro-carbonyls are rather uncommon [44] as underlined also in an interesting study carried out by Aubke et al. [45]. This group succeeded in the isolation and characterization of the first fluoro-carbonyl derivative of platinum: in their attempts to synthesize $[PtF_2(CO)_2]$, the reaction of PtF_6 with CO in liquid HF produced the mixed-valence product $[Pt(CO)_4][PtF_6]$, according to Eq. (21).

$$2PtF_6 + 7CO \rightarrow [Pt(CO)_4][PtF_6] + 3COF_2 \quad (21)$$

$[Pt(CO)_4][PtF_6]$ contains the homoleptic planar cation $[Pt(CO)_4]^{2+}$, which has been structurally characterized in the salt $[Pt(CO)_4][Sb_2F_{11}]_2$ [9a]. The IR active CO stretching vibration associated with this cation is observed in the range 2220–2250 cm^{-1}. Some attempts of synthesis of fluoro-carbonyls of platinum that met with failure are interesting: [*cis*-$PtCl_2(CO)_2$] does not react with HF, as expected on the base of the high HF BDE, whereas $[Pt(CO)_4][Sb_2F_{11}]_2$ reacts in liquid HF with CsF with evolution of CO, COF_2 and formation of $Cs[SbF_6]$ and anionic clusters of the type $[Pt_3(CO)_6]_n{}^{2-}$, according to a process schematized by Eq. (22).

$$3[Pt(CO)_4[Sb_2F_{11}]_2 + 14CsF$$

$$\rightarrow\ 1/n\{Cs_2[Pt_3(CO)_6]\}_n + 4COF_2 + 2CO\ +\ 12Cs[SbF_6] \qquad (22)$$

A possible justification of this outcome is that the introduction of CsF in HF enhances the basicity of the medium and promotes the attack of F^- to the strongly electrophilic carbon atom of the coordinated CO: we can suppose this is the first step to the formation of COF_2. In a similar way CO reduces platinum(II) with the assistance of H_2O and formation of CO_2.

The complete vibrational analysis of $[PtCl_2(CO)_2]$ has been reported and experimental data either of the solid product or of its molecules in solid argon matrix have been compared with the calculated values [45b].

Among the platinum(II) halo-carbonyls containing additional ligands, complexes with alkenes or alkylnitriles or carbenes have been isolated and characterized. The products [*cis*-PtX_2(CO)(alkene)] (X = Cl, Br; alkene = cyclohexene, cycloheptene [46a,b]; X = Cl, alkene = 1-octene [46c]) were produced by reaction of [*cis*-$PtX_2(CO)_2$] with an excess of the alkene (Eq. (23)) or by reaction of the dinuclear $[Pt_2(\mu\text{-}X)_2X_2(CO)_2]$ with the alkene (Eq. (24)).

$$[cis\text{-}PtX_2(CO)_2] + \text{alkene} \rightleftharpoons [cis\text{-}PtX_2(CO)(\text{alkene})] + CO \qquad (23)$$

$$[Pt_2(\mu\text{-}X)_2X_2(CO)_2] + 2\text{alkene} \rightarrow 2[cis\text{-}PtX_2(CO)(\text{alkene})] \qquad (24)$$

The two geometrical isomers of $[PtCl_2(CO)(NCEt)]$ were prepared by reacting either [*cis*-$PtCl_2(CO)_2$] with EtCN or $[PtCl_2(NCEt)_2]$ with CO (Eqs. (25) and (26)) [47].

$$[cis\text{-}PtCl_2(CO)_2] + NCEt \rightleftharpoons [PtCl_2(CO)(NCEt)] + CO \qquad (25)$$

$$[PtCl_2(NCEt)_2] + CO \rightarrow [PtCl_2(CO)(NCEt)] + EtCN \qquad (26)$$

Reactions (23) and (25) are equilibrium processes, well displaced on the left under CO at room temperature, as will be discussed in Section 4.

The complexes $[PtCl_2$(CO)(carbene)], carbene = 1,3-diethylimidazolidin-2-ylidene, 1,3-dibenzylimidazolidin-2-ylidene or 1,3-di(4-pentenyl)imidazolidin-2-ylidene [48] were obtained by transfer of carbene and carbonyl ligands from a tungsten carbene-carbonyl complex (see Scheme 1).

$$[PtCl_2(NCPh)_2]\ +\ [W(CO)_5(\text{carbene})] \longrightarrow$$

$$\longrightarrow [PtCl_2(CO)(\text{carbene})]\ +\ \text{products}$$

Scheme 1.

The treatment of $[PdCl_2(NCPh)_2]$ with $[W(CO)_5$(carbene)] does not afford $[PdCl_2$(CO)(carbene)], but the dinuclear $[Pd_2Cl_4(\text{carbene})_2]$ or the mononuclear biscarbene $[PdCl_2(\text{carbene})_2]$, no CO transfer being observed.

The family of the halo-carbonyls of palladium(II) has been enriched by the derivatives $[PPh_3Bz]$[*cis*-$PdCl_2R(CO)$] R = C_6H_3Me-2,NO_2-6 or $C_6H_2(NO_2)_3$-2,4,6) [49], interesting examples of stable aryl-carbonyl complexes of palladium(II). Moreover, although they do not belong to the group of the halo-carbonyls, [*cis*-$Pd(SO_3F)_2(CO)_2$] [50] and $[Pd(CO)_4][Sb_2F_{11}]_2$ [9a], deserve to be mentioned, as rare cases of palladium(II) complexes containing more than one CO ligand per metal atom.

Among the halo-carbonyls of palladium(I) and platinum(I), salts containing the anions $[M_2Cl_4(CO)_2]^{2-}$ (M = Pd, Pt) were well characterized [51]: the palladium anion shows a $[Pd_2(\mu\text{-}CO)_2]$ core, while no bridging ligands are present in the platinum species, the two $[PtCl_2(CO)]$ units being connected by a metal–metal bond. The derivative [PdCl(CO)] is known [20 and references therein, 52], although it is not structurally characterized. On the basis of its low solubility in the usual organic solvents and of its IR spectrum ($\tilde{\nu}_{CO}$ 1975 cm^{-1}), it is supposed to be a polynuclear compound with tetracoordinated palladium centres connected by alternate CO and Cl double bridges. At P_{CO} = 1 atm it does not adsorb further CO and reacts with $[NR_4]Cl$ yielding $[NR_4]_2[M_2Cl_4(CO)_2]$, containing the aforementioned dinuclear anion. The preparation of mixed-valence derivatives with formula $[PPN]_2[Pd_2(\mu\text{-}CO)_2Br_n(CO)_m]$ ($n + m = 4$) by substitution of Cl^- with Br^- in $[Pd_2(\mu\text{-}CO)_2Cl_4]^{2-}$ has been reported [53]. Single-crystal X-ray diffraction studies show a disordered structure of the anions, containing the $Pd_2(\mu\text{-}CO)_2$ fragments.

Kalck and co-workers have isolated and characterized a series of palladium(I) chloro-carbonyl species containing the $Pd_2(\mu\text{-}CO)_2$ core [54]. $[PBu_4]_2[Pd_2(\mu\text{-}CO)_2Cl_4]$ was prepared by carbonylation of $[PBu_4]_2[Pd_2Cl_6]$ and used as precursor of other palladium(I) carbonyl complexes. Calculations aimed to understand the nature of the bond between the two metal centres have been carried out. It appears that the pairing of the two lonely electrons on the d^9 centres is due to the delocalization along the CO bridging ligands [54].

Some recent examples of halo-complexes of palladium in low oxidation state are $[Pd_3(\mu_3\text{-}X)(\mu_3\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)][O_2CCF_3]$, X = Cl, Br, I [55] and $[Pd_{12}\ (\mu_3\text{-}I)_2(\mu_4\text{-}I)_3(\mu_2\text{-}CO)_6(PEt_3)_6][PF_6]$ [56].

3. Structures

General metric data used for comparison are referred to Cambridge Crystallographic Data Base [57].

While new solid state structural data concerning gold halo-carbonyls have not been published, the relatively high number of molecular and crystal structures of halo-carbonyl complexes of palladium and especially of platinum reported since 1990 imposes a selection. Here, only the structure of mono- and homo-dinuclear derivatives, with monodentate ligands and no disorder, will be discussed.

Starting from the highest metal oxidation number, the species $[NBu_4]$[*trans*-$PtBr(C_6F_5)_4(CO)$] is reported, which represents, according to the authors, the first structurally characterized platinum(IV) carbonyl [38]. In the anion (see Fig. 1) the platinum centre is hexacoordinated with octahedral geometry, as expected in a Pt(IV) complex.

The high oxidation state and the high coordination numbers of the metal are expected to act in opposite directions on the Pt–ligand bond distances. Pt–CO bond distance, 192.3 pm, is placed among the longest ones encountered in the majority of the four-coordinated Pt(II) compounds. The Pt–Br bond distance of 247.9 pm is slightly longer than the range 242.5–246.7 pm of distances found for the terminal bromides in the anion $[Pt_2Br_9]^-$ [58], probably because of the hindrance of pentafluorophenyl ligands.

In the larger family of the Pt(II) and Pd(II) halo-carbonyls, the molecular and crystal structure of [*cis*-$PtCl_2(CO)_2$] [39a] and of [*cis*-$PtBr_2(CO)_2$] [39b] (Fig. 2) have been determined. They are both square planar with comparable Pt–CO mean bond distances: 189.7 and 189.3 pm, respectively. The Pt–halide mean bond distances are 229.2 pm for Cl and 241.5 pm for Br, in keeping with those found in other Pt(II) halo-carbonyls which we will deal with later. The planar shape of these molecules allows stacking in the crys-

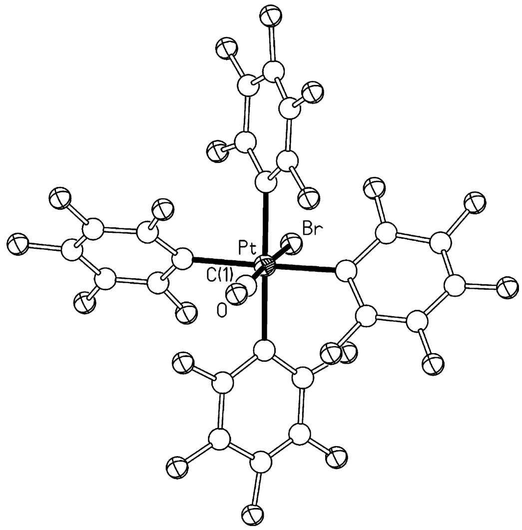

Fig. 1. Molecular structure of the anion $[PtBr(C_6F_5)_4(CO)]^-$.

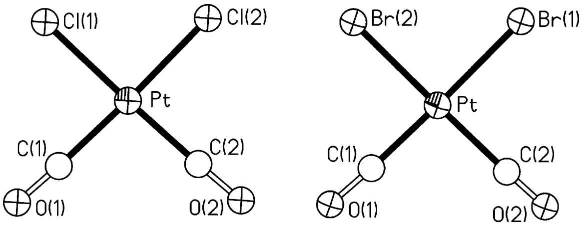

Fig. 2. Molecular structures of $[PtCl_2(CO)_2]$ and $[PtBr_2(CO)_2]$.

tals. The [*cis*-$PtCl_2(CO)_2$] molecules dispose in columns parallel to the **c** direction with a stacking step of 337.8 pm, while in [*cis*-$PtBr_2(CO)_2$] the columns are alternatively parallel to **a** and to **b** directions with 363.6 pm as mean stacking step. Both these distances are markedly longer than the Pt–Pt bond distance 277.4 pm found in the metal [59]. A view of the two layouts is shown in Fig. 3. In [*cis*-$PtCl_2(CO)_2$], the C···Cl distances between the carbonyl of a molecule and the chloride of the closer ones in the stack are slightly shorter than the sum of the respective van der Waals radii. The shortest C···Cl contact in [*cis*-$PtCl_2(CO)_2$] is in fact 333.3 pm, while the sum of the van der Waals radii is estimated about 345–350 pm, following the accepted compilations of these values [60]. These short contacts suggest the presence of intermolecular interactions. Abnormally short contacts, however, are not present in the stacks of [*cis*-$PtBr_2(CO)_2$], where the shortest C···Br distance is 358.7 pm.

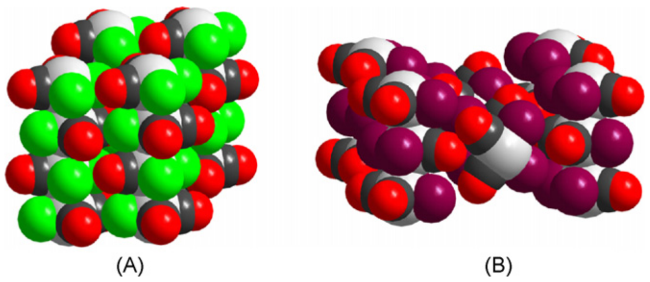
(A) (B)

Fig. 3. Stacking in parallel columns of $[PtCl_2(CO)_2]$, (A), and in layers of columns alternatively parallel to a and to b directions in $[PtBr_2(CO)_2]$, (B). Cl Atoms: Cl: green; Br: purple; O: red; C: black; Pt: white.

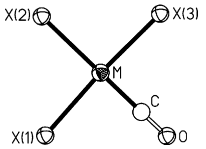

Fig. 4. Molecular structure of anions $[MX_3(CO)]^-$, M = Pd, Pt; X = Cl, Br, I.

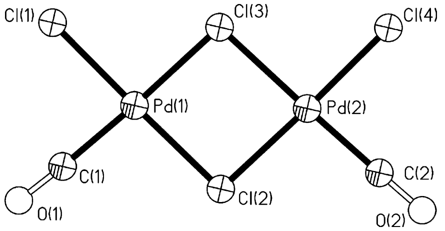

Fig. 5. Molecular structure of $[Pd_2Cl_4(CO)_2]$.

Similar to the molecular structures just described are those of the anions $[MX_3(CO)]^-$ (M = Pt; X = Cl, Br, I; M = Pd, X = Cl, Br) whose general shape is shown in Fig. 4. By attending only to those reported after 1990, $[PtBr_3(CO)]^-$ [38,39b,61] and $[PtI_3(CO)]^-$ [62] can be cited. The salts, which contain rather large monocharged cations, show anions with the expected square planar coordination. The reported Pt–CO bond distance is 182.2 pm in [PPN][$PtI_3(CO)$] [PPN^+ = bis(triphenylphosphine)imminium] and ranges between 183.0 and 185.5 pm in $[PtBr_3(CO)]^-$ in dependence of the cation nature and/or of the temperature [38,39b,61]). A comparison with the structure of [NBu_4][$PtCl_3(CO)$] (Pt–CO 182.5 pm) [63] shows that the Pt–CO distances do not vary significantly in the series. The Pt–X bond distances vary within very narrow ranges for each compound without significant differences among *trans* and *cis* positions with respect to CO. A comparison with the metric data of [NBu_4][PdX_3CO)] (X = Cl, Br) [12b] shows that the Pd–CO distances, 187 pm in both derivatives, are slightly but not significantly longer than the Pt–CO ones and do not vary with the nature of X. Also in the palladium anions the three Pd–X bond distances are independent of their position with respect to CO.

In order of growing complexity, the dinuclear species $[M_2Cl_4(CO)_2]$, M = Pd [39b], Pt [39b,64] have been structurally characterized. The palladium compound, which has been obtained in the *cis* conformation, shows the planar structure sketched in Fig. 5 with the metal adopting the usual pseudo square coordination. The carbonyl ligand of this compound displays rather short Pd–CO distances, 188 and 189 pm. The Pd–Cl distances are 226.1 pm for the terminal chloride, while for bridging chlorides the mean value 233.1 pm is in keeping with those found in polynuclear $PdCl_2$ structures [42,65]. The platinum compound, whose molecular structure [39b] is shown in Fig. 6, has been obtained in the *trans* conformation similarly to the already known $[Pt_2I_4(CO)_2]$ [12a]. The molecule is planar as for the palladium compound of Fig. 5, but shows an inversion centre. There are rather short Pt–CO distances, 185.2 pm, and a short terminal Pt–Cl distance of 212.3 pm. The bridging chlorides show two rather different bond distances; that of the halide *trans* to CO being shorter (228.4 pm) than that of the halide *trans* to the terminal chloride (239.2 pm). *trans*-$[Pt_2Cl_4(CO)_2]$ differentiates in the crystal packing from the other two dinuclear halo-carbonyls

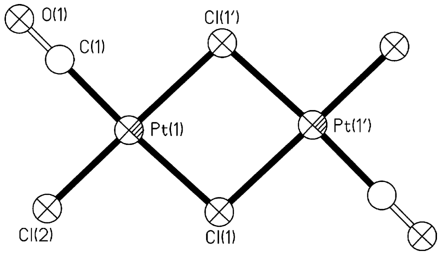

Fig. 6. Molecular structure of $[Pt_2Cl_4(CO)_2]$.

Table 1
$[PtX_2(CO)L]$ derivatives structurally characterized.

	Isomer	X	L	Pt–CO (pm)	Fig	References
1	*cis*	Cl	CO	189.7	2	[39a]
2	*cis*	Br	CO	189.3	2	[39b]
3	*cis*	Cl	NCEt	187.5	7A	[47]
4	*cis*	Cl	cy-heptene	185.1	8A	[46b]
5	*cis*	Br	cy-heptene	188.0	8A	[46b]
6	*cis*	Cl	Et_2carbene	184	8B	[48a]
7	*cis*	Cl	Bz_2carbene	183	8B	[48b]
8	*trans*	I	Dmphen	181.3	7B	[66]

Et_2carbene: 1,3-diethylimidazolidin-2-ylidene; Bz_2carbene: 1,3-dibenzylimidazolidin-2-ylidene; dmphen: 2,9-dimethyl-1,10-phenanthroline.

just mentioned, as it makes stacks of perfectly eclipsed molecules parallel to **c** direction with a stacking step of 352.5 pm.

A series of structurally characterized mononuclear neutral Pt(II) complexes with general formula $[PtX_2(CO)L]$ (X = halide, L = neutral ligand) is reported in Table 1, together with the values of the Pt–CO bond distance. The list contains the aforementioned [*cis*-$PtCl_2(CO)_2$], and [*cis*-$PtBr_2(CO)_2$], (items 1 and 2). Among the eight species, seven (items 1–7, X = Cl or Br) show the two halides in *cis* position while one (item 8, X = I) presents *trans* symmetry. Although the isolation in the solid state of a specific isomer cannot be considered the proof of its greater stability with respect to the other isomer, it is reasonable to think that it is not by chance that the diiodide shows the *trans*-isomer, unlike the dichlorides and dibromides. As a matter of fact, in the series $[PtX_2(CO)_2]$ the *cis* isomer appears to be more stable than the *trans* one for X = Cl, Br [39b], while the contrary is true for X = I [12a].

Two of the derivatives of Table 1 contain a N-donor ligand, propionitrile (item 3) or 2,9-dimethyl-1,10-phenanthroline (dmphen, item 8). The molecular structure of [*cis*-$PtCl_2$(CO)(NCEt)] [47] is shown in Fig. 7A. The essentially planar shape of this molecule allows a regular stacking which develops parallel to **c** with a stacking step of 3.364 Å (*c*/2). In [*trans*-PtI_2(CO)(dmphen)] [66], the phenanthroline, usually bidentate behaves as a monodentate ligand (Fig. 7B). In the latter example the Pt–CO bond makes with the Pt–N bond an angle of 162.7° being almost perpendicular to the Pt–I bonds (86.1°, 87.8°). The product is characterized by a rather short Pt–CO distance (181.3 pm) and a relatively long Pt–N bond distance (216.4 pm), while the Pt–I bond distances (262.5 and 262.6 pm) are in the normal range.

About the derivatives where L is a C donor ligand, the molecular structure of [*cis*-PtX_2(CO)(η^2-cycloheptene)]; X = Cl, Br [46b] (items 4 and 5 in Table 1) is shown in Fig. 8A. They show an almost ideal square coordination if we refer to the mid point of the cycloheptene carbon atoms bonded to the metal. Normal values for Pt–CO, Pt–Cl, and Pt–Br bond distances are observed. Small (but significantly greater than the estimated standard deviations) differences in bond length, 3–5 pm, distinguish the halogen *trans* to the carbonyl from that *trans* to the olefin, the former being shorter.

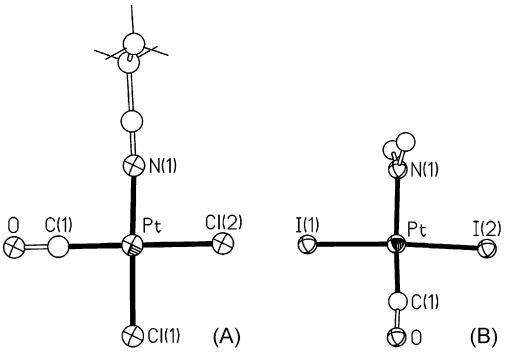

Fig. 7. Molecular structure of (A) $[PtCl_2(CO)(NCEt)]$ and (B) $[PtI_2(CO)$ 2,9-dimethyl-1,10-phenanthroline].

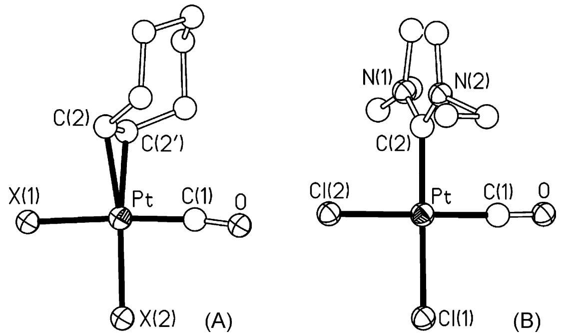

Fig. 8. (A) Molecular structure of $[PtX_2(CO)(\eta^2\text{-cycloheptene})]$; X = Cl, Br. (B) Molecular structure of alkylidene derivatives $[PtCl_2(CO)R]$; R = 1,3-diethylimidazolidin-2-ylidene, 1,3-dibenzylimidazolidin-2-ylidene.

Table 2
[PtXY(CO)L] derivatives structurally characterized (X *cis* to Y and *trans* to CO).

	X	Y	L	R_3	Pt–CO (pm)	Fig.	References
1	Cl	CH_3	PR_3	$(C_6F_5)_3$	182.1	9A	[67]
2	Cl	η^1-Cp	PR_3	$(C_6H_5)_2CH_3$	183.5	9A	[68]
3	CH_2CN	I	PR_3	$(\text{Cy-hexyl})_3$	191.9	9B	[69]
4	Cl	I	PR_3	$(\text{Cy-hexyl})_3$	189.5	9B	[69]

The coordination core of the complexes $[PtCl_2$(CO)(carbene)], carbene = 1,3-diethylimidazolidin-2-ylidene or 1,3-dibenzylimidazolidin-2-ylidene [48] (item 6 and 7, respectively, in Table 1) is shown in Fig. 8B. The Pt–C_{ol} (C_{ol} = olefinic carbon atoms), 219.2 pm and Pt–$C_{carbene}$ bond distances, 200.5 and 197.5 pm, respectively, fall in the normal range for these distances.

A second series of structurally characterized mononuclear neutral Pt(II) complexes, of general formula $[PtXY(CO)(PR_3)]$ (X, Y anionic ligands in mutually *cis* position, X *trans* to CO) is reported in Table 2.

The first group is that of $[PtClY(CO)(PR_3)]$; $R_3 = (C_6F_5)_3$, Y = CH_3 [67] (item 1 in Table 2); $R_3 = [(C_6H_5)_2(CH_3)]$, Y = σ-cyclopentadienyl [68] (item 2 in Table 2), whose molecular structure around the metal is shown in Fig. 9A. They show a Cl–Pt–CO angle ranging between 173.6° and 179.4°. The Pt–CO distances range between 182.1 and 187.5 pm while the Pt–Cl ones between 231.0 and 227.5 pm. Complexes having composition $[PtI(CO)(PR_3)X]$, (R = Cyclohexyl; X = CH_2CN, Cl; items 3 and 4, respectively, in Table 2) [69] are shown in Fig. 9B. The I–Pt–CO bond angle is 84.6° in the presence of the most hindering cyanomethyl ligand, and 91.2° when X = Cl. Pt–CO distances are 191.9 and 189.5 pm, respectively, slightly longer than the corresponding distances in the halo-carbonyls previously described. Also the Pt–I distances, 264.8, 267.4 pm, respectively, are longer than those present in iodo-carbonyls mentioned above, while Pt–Cl bond length falls in the usual range (231.6 pm).

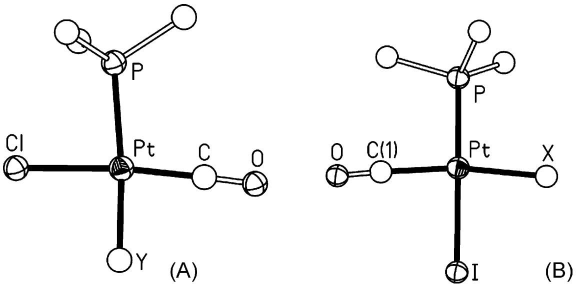

Fig. 9. Molecular structure of (A): $[PtClY(CO)(PR_3)]$, and (B): $[PtI(CO)(PR_3)X]$.

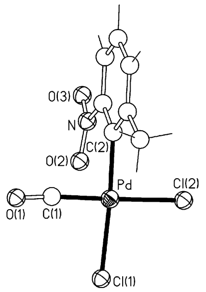

Fig. 10. Molecular structure of the anion $[PdCl_2(CO)(2\text{-methyl-6-nitrophenyl})]^-$.

The analysis of the Pt–CO bond distances in Tables 1 and 2 reveals a modest but not negligible excursion from 181.3 to 191.9 pm. The observed oscillations cannot be easily rationalized: probably several contributions co-operate to determine this parameter and among them, in addition to the electronic and steric features of the ligands, intermolecular interactions should not be neglected.

Before leaving the survey of M(II) halo-carbonyls we must consider the structure of the anion $[PdCl_2(CO)(2\text{-methyl-6-nitrophenyl})]^-$ [49] (Fig. 10). Its bond lengths and angles are similar to those found in alkylidene chloro-carbonyls of Pt(II) shown in Fig. 8B. The Pd–aryl distance is, in fact, 200.0 pm and Pd–CO distance is 185.3 pm. Only the Pd–Cl distances range between slightly longer values: 231.2–239.3 pm, the longer one being that *trans* to the aryl group.

In the end we must consider the structures of Pd(I) and Pt(I) halo-carbonyls. In this type of compound the electronic configuration of the metal ion allows the presence of a metal–metal bond. Structures which have been reported before 1990, concern dinuclear species like the anions $[M_2Cl_4(CO)_2]^{2-}$ [51b,d] and the neutral species of general composition $[M_2X_2(CO)_2L_2]$; X = Cl or Br, L_2 corresponding to $(PR_2R')_2$ (M = Pt) or $Ph_2ECH_2EPh_2$ (E = P, As, M = Pd) [70,71]. More recently the structure of the derivative $[Pt_2Cl_2(CO)_2(PFc_2Ph)_2]$ Fc = ferrocenyl have been reported [72], but it is not described here due to the presence of a second metal centre.

The anion $[Pd_2Cl_4(CO)_2]^{2-}$ has recently been studied again [73] (see Fig. 11). In this diamagnetic anion the distance between the palladium centres is 269 pm compared with 274.8 pm found in metallic Pd [74]. The bridging CO is found at distances ranging within 198–200 pm from the metal with Pd–C(O)–Pd angles of about 85°. Metric data concerning $[Pd_2Br_4(CO)_2]^{2-}$ [53] are not presented due to disorder in the structure. Several structurally characterized palladium(I) carbonyls contain the $Pd_2(\mu\text{-}CO)_2$ core [51b,53,73,75]. An exception is the species $[Pd_2(\mu\text{-}Cl)_2(CO)_4]$ obtained as air-stable crystals by $PdCl_2$ in anhydrous methanol under CO (in the presence of $NaHCO_3$ and 2-(1,5-dimethyl-4-hexenyl)-3-hydroxy-5-methyl-1,4-benzoquinone) [76]. The IR and structural data are nearly identical to those of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ [77], i.e. a bent $Pd_2(\mu\text{-}Cl)_2$ core and four terminal CO ligands. A theoretical study [78] dedicated to calculations concerning the possible different conformations of this species has appeared.

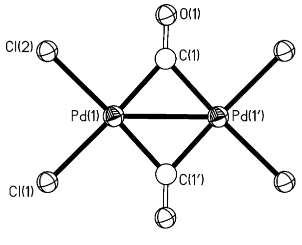

Fig. 11. Molecular structure of $[Pd_2Cl_4(CO)_2]^{2-}$.

4. Reactivity

The reaction of [AuCl(CO)] with ^iPrI has been anticipated in Section 2. Metallic gold and iodine were produced, according to Eq. (27) [12c,d] without any evidence of formation of [AuI(CO)], expected according to Eq. (28). This outcome denotes the instability of AuI with respect to the elements and a catalytic effect of CO in its decomposition. A suspension of AuI in CH_2Cl_2 remains unaltered in the absence of CO, but undergoes decomposition to Au and I_2 once CO is admitted into the reactor.

$$[AuCl(CO)] + {}^iPrI \rightarrow Au + CO + 1/2I_2 + {}^iPrCl \qquad (27)$$

$$[AuCl(CO)] + {}^iPrI \;\cancel{\longrightarrow}\; [AuI(CO)] + {}^iPrCl \qquad (28)$$

The study of some reactions of [AuCl(CO)] with HSR and Na[SR] [79] has shown that the CO is evolved. With HSR (R = ^tBu, 2,6-$(Me)_2C_6H_3$, C_6F_5) the formation of AuSR, according to Eq. (29) was observed. Analogously, the reaction with H_2S proceeds with evolution of CO and HCl and precipitation of Au_2S. It is reasonable that the formation of the strong H–Cl bond is the driving force of these reactions.

$$[AuCl(CO)] + HSR \rightarrow AuSR + CO + HCl \qquad (29)$$

The reaction of [AuCl(CO)] with $Na[S^tBu]$ in the presence of 15-crown-5 as Na^+ scavenger affords $[Na(15\text{-crown-}5)][{}^tBuS(AuCl)_3]$ (see Eq. (30)). In the product the anion contains a thiolate ligand bridging three AuCl units with formation of a tetrahedral arrangement ($RSAu_3$) around the sulphur atom. In this case Cl^- has no convenient alternative partner to bind to and its bond with gold is maintained.

$$3[AuCl(CO)] + Na(S^tBu) + 15\text{-crown-}5$$
$$\rightarrow [Na(15\text{-crown-}5)][tBuS(AuCl)_3] + 3CO \qquad (30)$$

The photochemistry of [AuCl(CO)] has been investigated [80]. Absorptions at 208, 220 and 250 nm are observed in solution (MeCN). While [AuCl(CO)] solutions are not photoluminescent, the solid compound shows an orange–red emission (663 nm). Irradiation in solution is accompanied by decomposition with formation of colloidal gold and $AuCl_3$. It is suggested that the photodecomposition proceeds with release of CO and transient formation of AuCl followed by disproportionation. A more recent paper [81] reports the results of experimental and computational studies of the molecular spectroscopy and bonding in [AuCl(CO)] in both solution (CH_3CN) and solid state, with the aim to contribute to a better understanding of the structure-luminescence relationship in linear gold(I) complexes. Absorption spectra (in the range 190–300 nm) of acetonitrile solutions of different concentrations suggest oligomerization of [AuCl(CO)], probably the formation of a dimer, when the concentration increases. Photoluminescence excitation and emission spectra of frozen solutions (CH_2Cl_2, 77 K) corroborate the hypothesis that progressive aggregation of the [AuCl(CO)] takes place in solution as the concentration increases.

A kinetic study concerning the CO exchange in $[PdCl_3(CO)]^-$ and $[PtX_3(CO)]^-$ X = Cl, Br) complexes is a useful source of data for a comparison between palladium(II) and platinum(II) derivatives containing π-acid ligands [82a]. A common associative mechanism with a five-coordinated transition state is assumed, the exchange being first order in both complex and CO concentration and the activation entropy being negative for all three cases. The CO exchange in $[PdCl_3(CO)]^-$ is about 200 times faster than in the corresponding platinum complex [*k:* $0.57 \pm .07$ and $(3.3 \pm 0.3) \times 10^{-3}\,dm^3\,mol^{-1}\,s^{-1}$ for Pd and Pt, respectively in $CDCl_3$, $T = 298$ K], to be compared with a rate ratio of about 1 for the ethene exchange rate in the complexes $[MCl_3(C_2H_4)]^-$ (M = Pd, Pt) [*k:* $(1.3 \pm 0.2) \times 10^3$ and $(9.0 \pm 1.1) \times 10^2\,dm^3\,mol^{-1}\,s^{-1}$ for Pd and Pt, respectively in THF-d_8) [82b]. In terms of kinetic comparison, in the complexes $[MCl_3L]^-$ (M = Pd, Pt; L = CO, C_2H_4), once the metal centre is fixed, the ethene exchange is always faster than the carbonyl exchange, the kinetic constant ratio being about 3×10^5 for platinum and 2×10^3 for palladium.

Platinum derivatives of the type [*cis*-$PtX_2(CO)(alkene)$] (X = Cl, Br) were prepared by substitution of CO in [*cis*-$PtX_2(CO)_2$] (Eq. (23)) or by splitting the halide bridge in $[Pt_2(\mu\text{-}X)_2X_2(CO)_2]$ with the alkene (Eq. (24)) [46], as seen in Section 2. The complexes [*cis*-$PtX_2(CO)(alkene)$] are unstable in the presence of CO, equilibrium 23 being shifted to the left at room temperature and atmospheric pressure of CO. The competitive coordination of CO and alkenes to transition metal centres is connected with a large number of catalytic processes involving both reagents, like alkene hydroformylation or CO/alkene copolymerization. Recently the thermodynamic parameters of the equilibria 31 and 32 have been reported [46c]. The equilibrium constants are $(2.4 \pm 0.5) \times 10^{-3}$ and $(2.8 \pm 0.4) \times 10^{-2}$, respectively. In both cases the displacement of CO is slight endothermic (ΔH° about 30 kJ mol^{-1}). The slight preference for 1-octene with respect to cyclohexene appears to depend mainly on entropy. If the solvation enthalpies of reagents and products are assumed to be similar, the positive ΔH° associated with these reactions can be considered mainly to arise from the rupture of the Pt–CO bond and the formation of the Pt–alkene bond. Thus, the former is about 30 kJ mol^{-1} stronger than the latter. The complete displacement of coordinated CO by the dienes COD and NBD, presumably arises from a favourable entropy change, two CO molecules being transferred to the gas phase [46c]. Data about the CO/alkene competition on palladium(II) [83] complexes were reported for $[Pd(phen)R(CO)]^+/C_2H_4$ (phen = 1,10-phenanthroline) system. Carbon monoxide is largely preferred with respect to ethylene, the equilibrium constant for the displacement of coordinated CO being $(2 \pm 1) \times 10^{-4}$ (T = 298 K, R = Me).

$$[cis\text{-}PtCl_2(CO)_2] + \text{cyclohexene} \rightleftharpoons [cis\text{-}PtCl_2(CO)(\text{cyclohexene})] + CO \qquad (31)$$

$$[cis\text{-}PtCl_2(CO)_2] + \text{1-octene} \rightleftharpoons [cis\text{-}PtCl_2(CO)(\text{1-octene})] + CO \qquad (32)$$

A kinetic study concerning reactions (31) and (32) [84] has indicated a rate law of the first order in both the complex and the alkene concentration. Also the large negative values of the activation entropy are consistent with an associative mechanism. In 1,2-dichloroethane, in the temperature range 273–308 K, reactions (31) and (32) show the following second-order rate constants at 298 K: cyclohexene, $(0.94 \pm 0.07) \times 10^{-3}$ M^{-1} s^{-1}; 1-octene, $(2.33 \pm 0.05) \times 10^{-2}$ M^{-1} s^{-1}. The activation parameters are, respectively: $\Delta H^* = (37 \pm 4)$ kJ mol^{-1}, $\Delta S^* = (-180 \pm 10)$ J K^{-1} mol^{-1} and $\Delta H^* = (36.5 \pm 0.7)$ kJ mol^{-1}, $\Delta S^* = (-154 \pm 2)$ J K^{-1} mol^{-1}. Both reverse reactions proceed with essentially the same rate constant (about 6×10^{-1} M^{-1} s^{-1}).

The competition between CO and propionitrile in chlorocomplexes of platinum(II) has been studied [47]. EtCN partially displaces coordinated carbon monoxide from [*cis*-$PtCl_2(CO)_2$] giving an equilibrium mixture of the two geometrical isomers of $[PtCl_2(CO)(NCEt)]$, together with unreacted [*cis*-$PtCl_2(CO)_2$], as monitored by IR and NMR measurements. The equilibrium has also been studied starting from $[PtCl_2(NCEt)_2]$, through displacement of coordinated EtCN by CO. The value of the equilibrium constant of reaction (33), measured at 23.4 °C, is $(2.1 \pm 0.3) \times 10^{-2}$, corresponding to $\Delta G^\circ = +9.5 \pm 0.3$ kJ mol^{-1}).

$$[cis\text{-}PtCl_2(CO)_2] + NCEt \rightleftharpoons [(cis + trans)\text{-}PtCl_2(CO)(NCEt)] + CO \qquad (33)$$

$$[PtI_2(CO)_2] + SO_2Cl_2 \longrightarrow [PtCl_2I_2(CO)_2] + SO_2$$
$$[PtCl_2I_2(CO)_2] \longrightarrow [cis\text{-}PtCl_2(CO)_2] + I_2$$

Scheme 2.

The reaction of the complexes $[PtCl_2(CO)(carbene)]$, carbene = 1,3-dialkylimidazolidin-2-ylidene [48] with PPh_3 proceeds with the substitution of CO and formation of $[PtCl_2(PPh_3)(carbene)]$. CO can be removed from $[PtCl_2(CO)(carbene)]$ also by treatment with Me_3NO with formation of $[PtCl_2(carbene)_2]$. When the alkyl substituents on the carbene contain a C=C function like in $[PtCl_2(CO)$(1,3-di(4-pentenyl)imidazolidin-2-ylidene)], thermal treatment (refluxing $CHCl_3$) produces an intermolecular CO displacement by the alkene, the carbene becoming bidentate [48b].

The reactions of the anions $[PtX_3(CO)]^-$ with AlX_3 (X = Cl, Br) has been partially discussed in Section 2 [39b]. When the process is carried out under CO, the kinetic product [*trans*-$PtX_2(CO)_2$] (Eqs. (8) and (18)) is obtained, which in a few hours isomerizes to the more stable *cis* isomer (Eqs. (9) and (19)). Under N_2 from $[PtCl_3(CO)]^-$ the dinuclear $[Pt_2(\mu\text{-}Cl)_2Cl_2(CO)_2]$ is produced according to Eq. (14). The dinuclear species reacts promptly with CO producing [*trans*-$PtCl_2(CO)_2$].

The already discussed reaction between [*cis*-$PtCl_2(CO)_2$] and ^iPrBr [39b] (Section 2, Eq. (20)) yields [*cis*-$PtBr_2(CO)_2$], the driving force arising from the formation of the strong C–Cl bond. Several examples of halide exchange which afford heavier halides of transition metals are known (see Eq. (34)) [43].

$$M^*X_n + n\,RY \longrightarrow M^*Y_n + n\,RX \qquad (34)$$

M* = transition metal or transition metal + ligands, X, Y = halide, X lighter than Y; R = H, alkyl

It can be suggested that the halide exchange occurs via formation of a transient adduct where RY is coordinated to the metal through the Y atom, followed by shift of R to X and elimination of RX. When [*cis*-$PtX_2(CO)_2$] is reacted with a nucleophile, the attack can be directed to the metal centre (with substitution or exchange of CO or Cl as discussed above) or to the carbon atom of the coordinated CO [13]. Among nucleophiles, water is able to perform the latter attack as shown for instance by the oxygen exchange between ^{18}O enriched water and the coordinated CO of $[PtCl_3(CO)]^-$ [85]. Data concerning the reaction of [*cis*-$PtX_2(CO)_2$] with water in definite molar ratios have been recently published [86]. By operating in toluene under CO the production of species analysing as $[PtCl(CO)]$ or $[Pt(CO)_2]$ is observed, in dependence of the water/platinum molar ratio. The reactions of gold, palladium and platinum chlorocarbonyls with water, which proceed with evolution of HCl and CO_2 and reduction of the metal centres are known, the metallic product nature depending on the reaction conditions [52,87].

An interesting case of nucleophilic activation of platinum(II) coordinated CO has been recently described [88] and deserves to be mentioned, although it concerns naphthyl-based PCP platinum(II) carbonyl cationic complexes and not halo-carbonyls: a rare platinum formyl complex, stabilized by the bulky tridentate ligand, was isolated and characterized.

Reactions affording the metal centre oxidation of halo-carbonyl complexes of palladium, platinum and gold are rare. The catalytic production of $COCl_2$ from CO and Cl_2 in the presence of gold chlorides [89] reasonably involve the oxidation of $[AuCl(CO)]$ by Cl_2. $[PtCl_2(CO)_2]$ does not react with Cl_2 in mild conditions, while $[PtCl_3(CO)]^-$ undergoes oxidation to $[PtCl_5(CO)]^-$ [89]. The reaction of $[PtI_2(CO)_2]$ with SO_2Cl_2, reported as a convenient preparation of $[PtCl_2(CO)_2]$ [39a,c] (Section 2, Eq. (10)), could proceed by oxidation to $[PtCl_2I_2(CO)_2]$, followed by reductive elimination of I_2 (Scheme 2).

The aforementioned reaction of [*cis*-$PtCl_2(CO)_2$] with ^iPrBr [39b] (see Eq. (20)) could proceed, alternatively to the hypothesis presented above, by oxidative addition of the alkyl bromide, followed by reductive elimination of RCl, although evidence of this type has not been obtained.

5. Catalysis

All three metal centres here considered are widely used in both heterogeneous and homogeneous catalyzed reactions. Catalysis by gold, which has been neglected in the past, has become a hot topic in recent years [90]. The recently reported catalytic production under mild conditions of carboxylic acids from alkenes, CO and H_2O in the presence of gold(I) in H_2SO_4 represents the first application of gold(I) carbonyls to organic syntheses [91]. A balanced competition between CO and alkene for the coordination to gold(I) is probably the determinant for the catalytic efficiency of the metal in processes involving the two building blocks: a study concerning this competition for the fragment AuCl had demonstrated that alkene (cyclooctene, norbornene) is slighter preferred to CO (Eq. (35)) with a value of the equilibrium constant about 4 in the case of norbornene at 22 °C in tetrachloroethane [92].

$$[AuCl(CO)] + \text{alkene} \rightleftharpoons [AuCl(\text{alkene})] + CO \qquad (35)$$

The catalyzed oxidation of CO to CO_2 is indeed interesting to solve the pollution problems caused by fuel incomplete combustion. Several recent data concerning the use of gold are present in the literature [93], although this field has been dominated for years by the use of palladium, platinum and rhodium supported on metal oxides as catalysts [94].

The study of CO oxidation over unreduced $PdCl_2$–$CuCl_2$ dispersed on Al_2O_3 or carbon [95] shows that the catalyst activity is enhanced by H_2O vapour. The authors suggest that, when H_2O vapour is present, the principal role of the copper is the re-oxidation of Pd(0) like in the Wacker process. Moreover they propose that, in the absence of H_2O vapour, copper appears to be involved in a reactive intermediate also containing Pd, CO and O_2. The chloro-carbonyls [PdCl(CO)] and [CuCl(CO)] were identified by IR and are supposed to be catalytically relevant. In the absence of water vapour an IR absorption at 2158 cm^{-1}, attributable to [$Pd_2Cl_4(CO)_2$] was observed.

Reactions of environmental importance are the reductions of NO operated by CO (see Eq. (36)). An aqueous system containing K_2PtCl_4, $CuCl_2$, CuCl and HCl has been studied as catalyst of reaction (36) [96] and mechanistic possibilities for the catalysis are discussed.

$$CO + 2NO \rightarrow N_2O + CO_2 \qquad (36)$$

The chloro-carbonyl anion $[PtCl_3(CO)]^-$, which is formed in the system [85], is considered a catalytic intermediate: it does not react to a significant extent with NO in the absence of the co-catalysts copper chlorides (both CuCl and $CuCl_2$ appear to be necessary), no fast carbonylation of $PtCl_4{}^{2-}$ and then no catalysis being observed in the absence of copper(I).

Catalytic hydrochlorination of terminal, internal and cyclic alkenes has been performed with the complexes [$PtCl_2(CO)$(alkene)] as catalytic precursors [46a]. With nonsymmetrical olefins Markovnikov addition was obtained. With cyclohexene-1,3,3-d_3 the production of the derivative of the syn-addition was observed, while the non-catalyzed reaction carried out in acetic acid affords the anti-addition product [97a,b]. On this basis, the addition of HCl is suggested to occur on the same side of the C=C moiety coordinated to platinum. Alkenes promptly react at room temperature with HBr or HI, but the addition of HCl usually requires higher temperatures, or the use of a catalyst [97c,d].

The formal addition of phosgene to allyl halides or mixture of ethylene and allyl chloride has been performed without the use of phosgene, by reacting the unsaturated substrate with CO and anhydrous HCl in the presence of $PdCl_2$. Chloroacylchlorides have been obtained which are good intermediates for the preparation of biologically active molecules. At the end of the cycles a solid corresponding to $[PdCl(CO)]_n$ is recovered [98]. The authors suggest that this polynuclear species is the catalyst precursor, its [$\cdots$ClPd(μ-CO)$_2$PdCl$\cdots$] units undergoing oxidative addition by RCl (R = H, allyl).

Maitlis and co-workers reported that palladium(II) and platinum(II) salts catalyze the carbonylation of MeI in MeOH to MeCOOMe [99], platinum derivatives being little less effective. PdI_2 proved to be an effective catalyst, once an excess of iodide is provided, without any other stabilizing ligand. When K_2PtCl_4 was used in the system {MeOH + MeI + CO + [Bu_4N]I} the IR spectrum of the final mixture showed a band at 2063 cm^{-1} attributable to $[PtI_3(CO)]^-$. Catalytic cycles involving either M(II)/M(IV) or M(0)/M(II) are suggested. The relevance of these studies is connected with the economic importance of the production of acetic acid (or its derivatives) from methanol and CO. The catalysts used in the industrial production of acetic acid are based on rhodium/iodide or promoted-iridium/iodide systems (BP-Monsanto process and the recent *Cativa* BP-Chemicals process, respectively, see references in [99]). As the iridium activity is low, a promoter must be added, and ruthenium complexes are used in the *Cativa* process. The study of a system based on [$Pt_2I_4(CO)_2$] as promoter has been recently reported by Kalck and co-workers [62]. Although the platinum complex alone does not catalyse the reaction, it is an efficient co-catalyst. The authors propose that its role is to extract an iodide ligand to the anionic $[IrI_3(Me)(CO)_2]^-$ and/or to scavenge iodide ions released in solution. In the course of this study the derivative [PPN][$PtI_3(CO)$] has been isolated and characterized by single-crystal X-ray diffraction methods as reported in Section 3.

Palladium catalyzed carbonylation of methanol in presence of alkali metal iodides as promoters was investigated. Palladium(II) acetate was used as catalyst precursor. By operating at 175 °C a high TOF value was obtained, provided that PPh_3 was added to the system to avoid precipitation of palladium black [100]. The intermediate salt $[MePPh_3]_2[Pd_2(\mu\text{-}I)_2I_4]$ was isolated and characterized by X-ray methods. In solution under CO the dinuclear anion is converted to $[PdI_3(CO)]^-$.

Among theoretical studies focused on important steps of catalytic cycles, one concerning the oxidative addition of C–H, C–C, and C–I bonds to uncoordinated Pd(0) and to the unknown square planar Pd(II) iodo-carbonyl [*cis*-$PdI_2(CO)_2$] has been performed at the ZORA-BP86/TZ(2)P level of relativistic density functional theory [101]. The calculated activation energies are always highest for C–C and decrease for C–H or C–I, but those of the palladium(II) complex induced reactions are 52–65 kcal mol^{-1} higher than those involving the uncoordinated palladium(0). The equilibrium geometry of [*cis*-$PdI_2(CO)_2$] has been calculated.

6. As molecular precursors to metal nanoparticles

Metal nanoparticles have attracted an extraordinary interest for their intrinsic properties and for their use in catalysis. Consequently, strategies aimed to their preparation and stabilization have become an important subject of research. In the field of noble metals, the use of halo-carbonyl complexes as precursors of metal nanoparticles appeared a good choice in view of the reducing properties of CO that are promoted by the presence of water, which allows the production of CO_2 and HX (see Section 3). As an example the reaction of [AuCl(CO)] is reported (Eq. (37)).

$$2[AuCl(CO)] + H_2O \rightarrow 2AU + CO_2 + CO + 2HCl \qquad (37)$$

As the metal particles form at room temperature and the accompanying products are volatile, this method allows one to work under particularly mild conditions, thus limiting coalescence phenomena. Metal nanoparticles on silica have been successfully produced using [AuCl(CO)] [102] or [*cis*-$PtCl_2(CO)_2$] [103] as precursors. The silica surface fixes the metal centres when treated with a solution of the precursor and the exposure of the material obtained to water vapour promotes the metal reduction.

The loading of silica with platinum or palladium was also carried out by using the molecular precursors [$Pt_2(\mu\text{-}Cl)_2Cl_2(CO)_2$], or [$Pd_2(\mu\text{-}Cl)_2Cl_2(CO)_2$], respectively [86]. The availability of the two analogous complexes was considered a good opportunity for a comparison of the behaviour of the two metal centres. The derivatives contain the required amount of coordinated CO to carry out the formation of the metal particles upon contact with moisture. The catalytic performances of the silica-supported platinum and palladium thus produced, were evaluated in the hydrogenation of cyclohexene, and appeared to be similar.

Unsupported gold nanoparticles have been produced through treatment of aqueous $HAuCl_4{\cdot}4H_2O$ with CO in ionic liquids [104].

7. Conclusions

The studies carried out in the last 20 years on the halo-carbonyls of palladium, platinum and gold allowed for some new synthetic methods of some already known derivatives and the preparation of new species. Among the new halo-carbonyls prepared by conventional methods, the derivative [$Pt(CO)_4$][PtF_6] is a rare example of metal fluoro-carbonyl and [NBu_4][$PtBr(C_6F_5)_4(CO)$] appears to be the first structurally characterized Pt(IV) carbonyl. In both derivatives the nature of the Pt–CO bond can be considered essentially σ.

The crystal and molecular structures of three important metal carbonyls of the family have been determined, namely [*cis*-$PtCl_2(CO)_2$], [$Pt_2(\mu\text{-}Cl)_2Cl_2(CO)_2$], and [$Pd_2(\mu\text{-}Cl)_2Cl_2(CO)_2$]. About the last derivative, its easy release of CO has allowed the growth of Pd_6Cl_{12} (β-$PdCl_2$) crystals, whose molecular structure has been determined by single-crystal X-ray diffraction methods.

The determination of thermodynamic and/or kinetic parameters of exchange or substitution reactions on these substrates is a matter of interest and the presence of coordinated carbon monoxide allows an easy monitoring of the reaction course by IR spectroscopy. Competition reactions between two different ligands for the same metal centre have been studied in the case of some platinum(II) systems ($PtCl_2LL'$; L, L′ = CO, alkene; CO, RCN). These studies deserve to be expanded not only to other combinations in the area of the platinum(II) complexes, which are the ideal choice for their moderate reaction rates, but also to palladium and gold systems.

The reactivity of the coordinated CO in these complexes is another important point to be explored: it can be exploited to drive the reduction of the metal in mild conditions, for instance by attack with water, or to assemble CO with other moieties, with formation for example of C–C, C–N or C–O bonds by reaction with the suitable nucleophiles.

In the field of heterogeneous and also homogeneous catalysis, the most striking aspect in the recent literature is the spectacular growth in studies involving gold. For the preparation of supported gold particles [AuCl(CO)] appears to be an interesting precursor as it can be easily loaded on a suitable support and reduced to metal in very mild conditions.

In conclusion, the chemistry of halo-carbonyls of palladium, platinum and gold continues to be an interesting subject of research. The reactivity of these derivatives, in part related to the large polarity of the M–CO bond, deserves to be further explored to improve the knowledge of the analogies and differences among these three metal centres and to gain useful information concerning their role in catalysis.

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