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Review

Halo-carbonyl complexes of palladium, platinum and gold

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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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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].

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

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).

$$Au_2Br_6 + 4CO \rightleftharpoons 2[AuBr(CO)] + 2COBr_2 \quad (2a)$$

$$CO + Br_2 \rightleftharpoons COBr_2 \quad (2b)$$

Because of the thermodynamic instability of $COBr_2$ with respect to CO + Br_2 (see Eq. (2b), $\Delta G^\circ = +26.3$ 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)).

$$AuBr + CO \rightarrow [AuBr(CO)] \quad (3)$$

$$Au_2Br_6 + 2C_6H_{10} \rightarrow 2AuBr + 2C_6H_{10}Br_2 \quad (4)$$

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