

# New routes to the synthesis of chloro-carbonyls of palladium(II) and platinum(II)

Daniela Belli Dell'Amico \*, Luca Labella

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

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Dedicated to Professor Fausto Calderazzo, on the occasion of his 70th anniversary, in recognition of his outstanding contributions to inorganic and organometallic chemistry.

## Abstract

$[\text{Pt}(\text{CO})_x]_n$  ( $x \sim 2$ ), the already described species obtained by the reaction of platinum(0) olefin complexes with carbon monoxide, reacts promptly at room temperature with  $\text{SO}_2\text{Cl}_2$  under CO affording *cis*- $\text{PtCl}_2(\text{CO})_2$ .  $[\text{Pd}_2(\text{CO})_y]_n$  ( $y \sim 1$ ), obtained by  $\text{Pd}(\text{dba})_2$  and CO at room temperature, reacts in the same conditions yielding  $\text{Pd}_2\text{Cl}_4(\text{CO})_2$ . Similarly, although more slowly, finely divided platinum and palladium, in the form of metal blacks, react with  $\text{SO}_2\text{Cl}_2$  and CO at room temperature producing again *cis*- $\text{PtCl}_2(\text{CO})_2$  and  $\text{Pd}_2\text{Cl}_4(\text{CO})_2$ , respectively. In the absence of CO no reaction is observed within 4 weeks. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Platinum black; Palladium black; Platinum carbonyl; Palladium carbonyl; Platinum chloride; Palladium chloride

## 1. Introduction

Palladium and platinum as metals are rarely used as reagents for the synthesis of metal salts or complexes in mild conditions, although platinum and palladium blacks [1] are both good examples of readily accessible finely divided metals. They are both used extensively as catalysts for many reactions [2]. Therefore, their relatively high (especially for platinum) atomization energy  $\{\Delta H^\circ(\text{Pt}_{(g)}) = 565.3 \text{ kJ mol}^{-1}$ ,  $\Delta H^\circ(\text{Pd}_{(g)}) = 378.2 \text{ kJ mol}^{-1}$  [3]}, does not prevent their interaction with several compounds. Some of the catalyzed processes involve carbon monoxide: focusing on the metal–CO interaction, it is worth to recall that, despite nickel, which belongs to the same group, reacts with CO in mild conditions affording  $\text{Ni}(\text{CO})_4$  [4], palladium and platinum tetracarbonyls have not yet been isolated by any synthetic method, but in matrix conditions [5]. Their assumed low stability has been attributed to a high metal atomization energy in the case of platinum

and to a low M–CO bond energy in the case of palladium [6].

As far as platinum is concerned, the system CO– $\text{H}_2\text{O}$  as a reductant of chlorocomplexes  $[\text{PtCl}_4]^{2-}$ ,  $[\text{PtCl}_2(\text{CO})_2]$  affords species of composition  $\text{Pt}(\text{CO})_2$  [7]. Although not sufficiently characterized, they deserve remarkable interest, in view of the above-mentioned lack of well-defined platinum binary carbonyls. A recently reported [8] black material of approximate composition  $[\text{Pt}(\text{CO})_2]_n$  (from now on we will refer to it using this formula) was obtained by reacting homoleptic olefin complexes of platinum(0) [9] with CO. Unlike the species reported before [7], this compound was found to be labile and to decompose with irreversible loss of carbon monoxide at reduced partial pressure of CO and/or at temperatures higher than about 0°C. Moreover, it was easily oxidized by iodine under CO atmosphere [8] with the formation of  $\text{PtI}_2(\text{CO})_2$ .

These results led us to enlarge our knowledge about the reactivity of this derivative and to test the chemistry of palladium in the same field. Moreover, for sake of comparison, we have also studied the reactivity in similar conditions of the metal blacks, prepared by the classical methods [10].

\* Corresponding author. Tel.: +39-050-918206; fax: +39-050-20237.

E-mail address: belli@dcci.unipi.it (D. Belli Dell'Amico)

## 2. Results and discussion

Among the homoleptic palladium olefin complexes [11], the well characterized derivatives  $\text{Pd}_2(\text{dba})_3$  (dba = dibenzylideneacetone) and  $\text{Pd}_3(\text{tbaa})_3$  (tbaa = tribenzylideneacetylacetone) are reported to react with CO with decomposition to palladium metal and free olefin [11d, e]. In our hands,  $\text{Pd}(\text{dba})_2$  prepared according to the literature [11f], reacted rapidly with CO ( $P = 1$  atm.) at room temperature in toluene or cyclohexane with uptake of carbon monoxide, corresponding to a molar ratio  $\text{CO}/\text{Pd} = 0.5$ , and formation of a black powder. This material,  $[\text{Pd}_2(\text{CO})_y]_n$  ( $y \sim 1$ ; we will refer to it with the formula  $[\text{Pd}_2(\text{CO})_n]$ ), whose nature we are currently exploring, decomposes easily with loss of CO. IR spectra of the product do not show any bands in the carbonyl stretching region: it is likely that decomposition occurs during the sample work up.

As part of an ongoing research program in the field of noble metal halo-carbonyl complexes, the derivatives  $[\text{Pt}(\text{CO})_2]_n$  [8] and  $[\text{Pd}_2(\text{CO})_n]$  have been used as reagents for the syntheses of chloro-carbonyls.

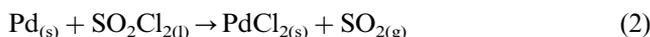
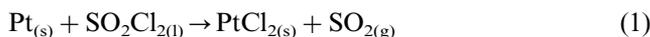
$[\text{Pt}(\text{CO})_2]_n$ , by reaction with  $\text{SO}_2\text{Cl}_2$  at room temperature under CO atmosphere, afforded rapidly *cis*- $\text{PtCl}_2(\text{CO})_2$  in good yield. The complete disappearance of the black reagent and the formation of a pale yellow solution are clear evidences of the completeness of the reaction. The product, recovered in high yield (92%), was characterized by IR spectroscopy ( $\bar{\nu}_{\text{CO}}$  at 2168 and  $2127 \text{ cm}^{-1}$  [12]).

Similarly,  $[\text{Pd}_2(\text{CO})_n]$  instantaneously reacted at room temperature with  $\text{SO}_2\text{Cl}_2$  under CO in  $\text{SOCl}_2$  as solvent, giving an orange solution of  $\text{Pd}_2\text{Cl}_4(\text{CO})_2$ . The IR spectrum showed a band at  $2163 \text{ cm}^{-1}$  [13] due to the CO stretching in the complex, whose absorbance corresponded to a yield of 94%.

The high reactivity of these materials is presumably related to their probable cluster-like structure and to their higher fragmentation in comparison with the bulk metal. On this basis, we considered it interesting to test the reactivity, if any, of the finely divided metals in analogous conditions and palladium and platinum blacks appeared to be suitable candidates to carry out these experiments. Although they are widely used in catalysis, there are not many studies on their morphology and structure [14]. They have been used as reagents in the synthesis of metal salts or complexes only with strong oxidants often at high temperature, an example being the preparations of the metal chlorides [15].

The metal blacks treated with  $\text{SO}_2\text{Cl}_2$  yielded, in the presence of CO ( $P = 1$  atm.), the above mentioned chloro-carbonyl products. Approximately 1 mmol of palladium was converted to  $\text{Pd}_2\text{Cl}_4(\text{CO})_2$  in 2 h at about  $25^\circ\text{C}$  operating in a solution of  $\text{SO}_2\text{Cl}_2$  in  $\text{SOCl}_2$  1:1 in volume. Platinum reacted in the same conditions about 100 times more slowly.

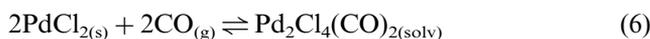
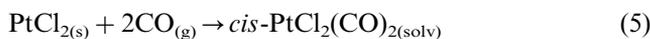
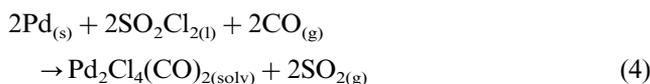
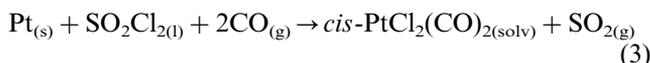
The use of sulphuryl chloride as an oxidant for platinum metals has been reported [15b]. Palladium black is converted to  $\beta\text{-PdCl}_2$  in 3 days at  $400^\circ\text{C}$  and platinum to  $\beta\text{-PtCl}_2$  in 7 days at  $450\text{--}500^\circ\text{C}$  or to  $\text{PtCl}_4$  in 7 days at  $350^\circ\text{C}$ . From a thermodynamic point of view, the formation of  $\text{MCl}_2$  ( $M = \text{Pd}, \text{Pt}$ ) from  $M$  and  $\text{SO}_2\text{Cl}_2$  (see Eqs. (1) and (2)) appears to be feasible at room temperature in both cases.



$\Delta H^\circ$  values of  $-13$  and  $-70 \text{ kJ mol}^{-1}$  are obtained for platinum and palladium, respectively, by the standard enthalpy formation of  $\text{SO}_2\text{Cl}_2$  ( $-394.1 \text{ kJ mol}^{-1}$  [3]),  $\text{SO}_2$  ( $-296.8 \text{ kJ mol}^{-1}$  [3]),  $\text{PtCl}_2$  ( $-110.5 \text{ kJ mol}^{-1}$  [16]) and  $\text{PdCl}_2$  ( $-166.8 \text{ kJ mol}^{-1}$  [16]). Moreover, these exoergonic reactions are entropically favored.

Nevertheless, our attempts to obtain  $\text{MCl}_2$  from the metal blacks and  $\text{SO}_2\text{Cl}_2$  in the absence of CO at room temperature met with failure. It is possible that insoluble metal chlorides initially formed on the surface protect the metals from further attack. This hypothesis does not contrast with our analytical data (at the end of the treatment only traces of chlorine were found in the black solids, once washed and dried) because the formation of metal chlorides on the particle surface (estimated medium diameter  $50 \text{ nm}$  [1b]) would require a negligible percentage of chlorine in the material.

As a matter of fact, the addition of CO modifies the chemical systems (see Eqs. (3) and (4)), and, in view of the well established stability of the chloro-carbonyl derivatives of platinum (see Eq. (5)) [17] and palladium (see Eq. (6),  $\Delta H^\circ = -57 \text{ kJ mol}^{-1}$ ;  $\Delta S^\circ = -129 \text{ J mol}^{-1} \text{ K}^{-1}$ ) [13], Eqs. (3) and (4) can be considered, at room temperature, more favored than Eqs. (1) and (2), respectively.



The first step of the process could be the formation of a surface metal chloride, followed by CO uptake to produce the metal chloro-carbonyls, as recently proposed [18] in the study of the reaction of a platinum film with a mixture of CO and  $\text{Cl}_2$ . Nevertheless, we cannot exclude that the reactions proceed by formation of surface metal carbonyls and subsequent chlorination. The rapid formation of the chloro-carbonyl complexes from  $[\text{Pt}(\text{CO})_2]_n$  or  $[\text{Pd}_2(\text{CO})_n]$  and  $\text{SO}_2\text{Cl}_2$  supports the latter hypothesis, although does not exclude the former.

### 3. Experimental

All preparations were carried out using standard Schlenk techniques. All organic solvents were freshly distilled over conventional drying agents under dinitrogen and all reactions were carried out under an atmosphere of dinitrogen, or carbon monoxide, as stated.  $\text{SO}_2\text{Cl}_2$  (Aldrich) and  $\text{SOCl}_2$  (C. Erba) were used as received. Platinum and palladium blacks [10],  $[\text{Pt}(\text{CO})_2]_n$  [8] and  $\text{Pd}(\text{dba})_2$  [11f] were prepared according to the literature. IR spectra were recorded on a FT-IR Perkin–Elmer mod. 1725X spectrophotometer. The molar extinction coefficients of the CO stretching vibration of *cis*- $\text{PtCl}_2(\text{CO})_2$  in toluene ( $2168\text{ cm}^{-1}$ ),  $\varepsilon = 1200\text{ mol}^{-1}\text{ l cm}^{-1}$  [12] and of  $\text{Pd}_2\text{Cl}_4(\text{CO})_2$  in  $\text{SOCl}_2$  ( $2163\text{ cm}^{-1}$ ),  $\varepsilon = 1415\text{ mol}^{-1}\text{ l cm}^{-1}$  [13] were used for yield determinations. The thickness of the cell ( $1.1 \times 10^{-2}\text{ cm}$ ) was determined by the interference method. Elemental analyses (C, H) were performed in the Laboratorio di Microanalisi, Facoltà di Farmacia, Università di Pisa, with a C. Erba mod. 1106 elemental analyzer. Chlorine analyses were performed according to Volhard method after attack of the samples with an excess of boiling aqueous solution of sodium formate.

#### 3.1. Reaction of $\text{Pd}(\text{dba})_2$ with CO

A suspension of  $\text{Pd}(\text{dba})_2$  (0.476 g, 0.83 mmol) in toluene ( $50\text{ cm}^3$ ) was saturated with CO ( $P = 1\text{ atm.}$ ) at room temperature. A rapid absorption of CO was observed. The black suspension was decanted, the solid was washed three times with cyclohexane and dried under carbon monoxide (0.083 g, 83% yield as  $[\text{Pd}_2(\text{CO})]_n$ ). Anal. Calc. for  $\text{CPd}_2\text{O}$ : C, 5.0%. Found: C, 4.1%. IR spectra registered on Nujol-mulls did not show any bands in the CO stretching region. The free ligand was recovered unchanged (IR comparison) from the filtrate in a 83% yield.

In a gasvolumetric experiment,  $\text{Pd}(\text{dba})_2$  (0.511 g, 0.89 mmol) in toluene ( $25\text{ cm}^3$ ) reacted with CO ( $P = 760\text{ torr}$ ) for about 3 min at  $T = 23^\circ\text{C}$  with a CO uptake corresponding to CO/Pd molar ratio 0.53.

#### 3.2. Reaction of $[\text{Pt}(\text{CO})_2]_n$ with $\text{SO}_2\text{Cl}_2$

A solution of  $\text{SO}_2\text{Cl}_2$  ( $0.20\text{ cm}^3$ ; 2.48 mmol) in toluene ( $20\text{ cm}^3$ ) was saturated with CO at room temperature and  $[\text{Pt}(\text{CO})_2]_n$  (0.172 g, 0.69 mmol) was added. After a few minutes, a yellow solution was obtained. An IR spectrum showed the bands of  $\text{PtCl}_2(\text{CO})_2$  at  $2168$  and  $2127\text{ cm}^{-1}$ . The absorbance of the former band was  $A = 0.42$ , corresponding to a 92% yield.

#### 3.3. Reaction of $[\text{Pd}_2(\text{CO})]_n$ with $\text{SO}_2\text{Cl}_2$

A solution of  $\text{SO}_2\text{Cl}_2$  ( $12.5\text{ cm}^3$ ) in  $\text{SOCl}_2$  ( $12.5\text{ cm}^3$ ) was saturated with CO and  $[\text{Pd}_2(\text{CO})]_n$  (0.026 g, 0.22 mmol of Pd) was added. A yellow solution was immediately obtained. An IR spectrum showed the band due to  $\text{Pd}_2\text{Cl}_4(\text{CO})_2$  at  $2163\text{ cm}^{-1}$  with an absorbance  $A = 0.064$ , corresponding to a 94% yield.

#### 3.4. Reaction of platinum black with CO and $\text{SO}_2\text{Cl}_2$

Platinum black (0.231 g, 1.18 mmol) was added to a solution of  $\text{SO}_2\text{Cl}_2$  ( $20\text{ cm}^3$ ) in  $\text{SOCl}_2$  ( $20\text{ cm}^3$ ) under CO atmosphere. After about 150 h, a pale yellow solution was obtained. The solution was evaporated to dryness and the residue was dissolved in toluene ( $51\text{ cm}^3$ ). An IR spectrum of the solution showed the bands due to *cis*- $\text{PtCl}_2(\text{CO})_2$  at  $2168$  and  $2127\text{ cm}^{-1}$ , the former with absorbance  $A = 0.28$ , corresponding to a 92% yield.

In another experiment platinum black (0.061 g, 0.31 mmol),  $\text{SO}_2\text{Cl}_2$  ( $10\text{ cm}^3$ ) and  $\text{SOCl}_2$  ( $10\text{ cm}^3$ ) were introduced in a tube ( $500\text{ cm}^3$  volume) under CO ( $P = 1\text{ atm.}$ ) The tube was flame-sealed and the suspension was stirred at  $60^\circ\text{C}$ . After 30 h, a pale yellow solution was obtained. The IR spectrum showed the band at  $2168\text{ cm}^{-1}$  due to *cis*- $\text{PtCl}_2(\text{CO})_2$  with an absorbance corresponding to a nearly quantitative yield.

#### 3.5. Reaction of palladium black with CO and $\text{SO}_2\text{Cl}_2$

Palladium black (0.045 g, 0.42 mmol) was added under CO to a solution of  $\text{SO}_2\text{Cl}_2$  ( $10\text{ cm}^3$ ) in  $\text{SOCl}_2$  ( $10\text{ cm}^3$ ). The suspension was stirred at room temperature. After 1 h, an orange solution was obtained. The IR spectrum showed the band at  $2163\text{ cm}^{-1}$  due to  $\text{Pd}_2\text{Cl}_4(\text{CO})_2$  with  $A = 0.16$  corresponding to a nearly quantitative yield.

#### 3.6. Treatment of platinum black with $\text{SO}_2\text{Cl}_2$

Platinum black (0.300 g, 1.54 mmol) was added under  $\text{N}_2$  to a solution of  $\text{SO}_2\text{Cl}_2$  ( $10\text{ cm}^3$ ) in  $\text{SOCl}_2$  ( $10\text{ cm}^3$ ). The suspension was stirred at room temperature for 30 days, and filtered. The black solid, washed several times with heptane and dried in vacuo, contained only traces of chlorine.

#### 3.7. Treatment of palladium black with $\text{SO}_2\text{Cl}_2$

Palladium black (0.088 g, 0.83 mmol) was added under  $\text{N}_2$  to a solution of  $\text{SO}_2\text{Cl}_2$  ( $10\text{ cm}^3$ ) in  $\text{SOCl}_2$  ( $10\text{ cm}^3$ ). The suspension was stirred at room temperature for 30 days, and filtered. The black solid, washed several times with heptane and dried in vacuo, contained only traces of chlorine.

#### 4. Conclusions

$[\text{Pt}(\text{CO})_2]_n$  [8] and  $[\text{Pd}_2(\text{CO})]_n$ , obtained by treating  $\text{Pd}(\text{dba})_2$  with CO, afforded smoothly *cis*- $\text{PtCl}_2(\text{CO})_2$  and  $\text{Pd}_2\text{Cl}_4(\text{CO})_2$ , respectively, by reacting with  $\text{SO}_2\text{Cl}_2$ .

Additionally, we have found that, although palladium and especially platinum are oxidized with difficulty in mild conditions, the metal blacks react at room temperature with  $\text{SO}_2\text{Cl}_2$  in the presence of CO producing the chloro-carbonyl complexes. No metal oxidation was observed in the absence of CO.

These reactions constitute new routes to the syntheses of chloro-carbonyls of palladium and platinum. Furthermore, the study of the reactivity of  $[\text{Pt}(\text{CO})_2]_n$  and  $[\text{Pd}_2(\text{CO})]_n$  can be useful to better understand the nature of these two elusive derivatives, which are interesting either as members of the binary metal carbonyl family, or as examples of transient species in processes going from molecular towards bulk metal materials [8].

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