

# Reactions of zerovalent olefin complexes of platinum with carbon monoxide<sup>☆</sup>

Daniela Belli Dell' Amico<sup>a</sup>, Fausto Calderazzo<sup>a,\*</sup>, Michael Dittmann<sup>b</sup>, Luca Labella<sup>a</sup>,  
Fabio Marchetti<sup>a</sup>, Eberhard Schweda<sup>b</sup>, Joachim Strähle<sup>b</sup>

<sup>a</sup> *Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, I-56126 Pisa, Italy*

<sup>b</sup> *Institut für Anorganische Chemie der Universität Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany*

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## Abstract

The reaction of platinum(0) olefin complexes with carbon monoxide at room temperature in hydrocarbon solvents was monitored gasvolumetrically and shown to give an unstable amorphous platinum(0) carbonyl derivative characterized by a CO:Pt molar ratio of 2 under the best conditions (low temperature, atmospheric pressure). The product of the olefin substitution by CO may be regarded as an intermediate towards the formation of platinum metal, whose diffraction pattern was detected upon heating the carbonylated product at about 250°C. The carbonylation product is highly reactive at room temperature towards di-iodine or the bidentate tertiary phosphine dppe giving PtI<sub>2</sub>(CO)<sub>2</sub> or Pt(dppe)<sub>2</sub>, respectively, in substantially quantitative yields. The present findings suggest the following relative affinity for platinum(0): dppe > CO > olefin. Steric congestion of the olefin ligands preventing the platinum atoms from readily forming metal–metal bonds presumably explains the experimentally established isolation of platinum(0) olefin complexes by Stone and coworkers. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Platinum carbonyls; Platinum olefin; Platinum cluster

## 1. Introduction

Platinum has played a fundamental role in organometallic chemistry: the first olefin, carbonyl and transition metal alkyl derivatives were synthesized with platinum as the central metal atom, in the oxidation states II and IV, namely the Zeise's salt, K[PtCl<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>)]·H<sub>2</sub>O [1a,b], *cis*-PtCl<sub>2</sub>(CO)<sub>2</sub> [1c,d], and the methyl derivatives Pt<sub>4</sub>I<sub>4</sub>Me<sub>12</sub> [1e,f]. In spite of this extensive research activity on the organometallic derivatives of platinum in its positive oxidation states, some important questions still remain unanswered as far as the chemistry of platinum(0) is concerned: which ligand, between carbon monoxide and olefin has the

higher affinity for platinum(0) and why molecular platinum(0) carbonyl derivatives are elusive species.

Booth and Chatt [2a] reported the synthesis of a purple (from K<sub>2</sub>PtCl<sub>4</sub>) or a brown (from Na<sub>2</sub>PtCl<sub>4</sub>) carbonyl product (with a CO:Pt molar ratio of approximately 2), of unknown nuclearity, formulated as [Pt(CO)<sub>2</sub>]<sub>n</sub>, by carbonylation of an aqueous chloroplatinate(II) solution. Moreover, by the action of water on a benzene solution of *cis*-PtCl<sub>2</sub>(CO)<sub>2</sub> in the presence of carbon monoxide, a product with an IR spectrum ( $\nu_{\text{CO}}$  at 2068 and 1891 cm<sup>-1</sup>) identical to that obtained from K<sub>2</sub>PtCl<sub>4</sub> was secured. Moreover, carbonyl-tertiary phosphine complexes of platinum(0) have been reported [2a,b] to be obtained by the addition of monodentate tertiary phosphines to the dicarbonyl product. Likewise, olefin complexes of zerovalent platinum have been used [2c–e] for the sequential treatment with tertiary phosphine and carbon monoxide for producing similar zerovalent compounds and finally, neutral platinum clusters formulated as Pt<sub>24</sub>(CO)<sub>30</sub>, Pt<sub>26</sub>(CO)<sub>32</sub>, and Pt<sub>38</sub>(CO)<sub>44</sub> have been identified spectro-

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\* Corresponding author. Tel.: +39-50-918218; fax: +39-50-20237.

E-mail address: facal@dcii.unipi.it (F. Calderazzo)

Table 1  
Reactions of platinum(0) olefin complexes with CO<sup>a</sup>

Starting material	Sample	Solvent	$M$ (mol l <sup>-1</sup> ) × 10 <sup>3</sup> <sup>b</sup>	$T$ (°C)	CO:Pt molar ratio <sup>c</sup>
Pt(C <sub>7</sub> H <sub>10</sub> ) <sub>3</sub>	LL201	Toluene	6.7	1.0	1.95
Pt(C <sub>7</sub> H <sub>10</sub> ) <sub>3</sub>	SC106	Cyclohexane	10.3	19.5	1.87
Pt(C <sub>7</sub> H <sub>10</sub> ) <sub>3</sub>	LL209	Toluene	7.2	25.0	1.90
Pt(C <sub>7</sub> H <sub>10</sub> ) <sub>3</sub>	LL192	Toluene	10.5	28.6	1.49
Pt <sub>2</sub> (dba) <sub>3</sub> · toluene	LL179	Cyclohexane	3.2	21.0	1.76
Pt(COD) <sub>2</sub>	LL182	Cyclohexane	5.3	20.6	1.62

<sup>a</sup> Gas volumetric data.

<sup>b</sup> Concentration of the platinum reagent.

<sup>c</sup> From the gasvolumetric CO absorption.

scopically during the voltammetric oxidation of the corresponding dianions [2f]. The carbonyl species [Pt(CO)<sub>2</sub>]<sub>n</sub> has not been sufficiently characterized, mainly due to its insolubility in all common solvents. Chini and coworkers [3] suggested that the dicarbonyl product could belong to the well-established class of the anionic platinum carbonyls [4], with [H<sub>3</sub>O]<sup>+</sup> as cationic counterpart. The lack of well-defined binary carbonyl complexes of zerovalent platinum contrasts with the existence of homoleptic platinum(0) olefin complexes, mainly thanks to the elegant studies of Stone and his coworkers [5]; these compounds have been completely characterized by conventional techniques, including X-ray- [5b–d] and neutron [5e] diffraction experiments. These observations are remarkable and somewhat intriguing: olefins should be regarded as weaker ligands than carbon monoxide for platinum(II) [6], coordinated olefin in complexes of the type *cis*-PtCl<sub>2</sub>(CO)(olefin) being promptly displaced by carbon monoxide at atmospheric pressure to give *cis*-PtCl<sub>2</sub>(CO)<sub>2</sub>. By extending earlier work by Maitlis [7] on the reaction between Pt(dba)<sub>2</sub> (dba = dibenzylideneacetone) and CO, Chaudret and Bradley and their coworkers [8a] found that carbon monoxide reacts with Pt(dba)<sub>2</sub> to give platinum nanoparticles (with a diameter of 1.2 or 1.5 nm, in the presence of nitrocellulose or cellulose acetate, respectively). On the other hand, the same platinum(0) substrate reacts [8b] with CO in toluene affording a brown precipitate, the latter giving a colloidal dichloromethane solution with nanoparticles comprised of between 1.0 and 2.0 nm.

In continuation of our studies on carbonyl derivatives of platinum and palladium [1d, 9], we thought it worthwhile to study the primary products of the carbonylation reaction of platinum(0) olefin complexes gasvolumetrically and extend the investigation to other substrates in addition to the dba complex, by operating under strictly anhydrous conditions. In this paper we have established the stoichiometry of the reaction of platinum(0) olefin complexes with carbon monoxide and we have collected some new spectroscopic data

allowing us to suggest that the primary product of the olefin displacement by carbon monoxide is an uncharged small cluster of platinum atoms containing both terminal and bridging carbonyl groups, characterized by a CO:Pt molar ratio of 2 under the best conditions of low temperature and atmospheric pressure of carbon monoxide. The product readily decomposes to larger platinum clusters and finally to platinum metal as the temperature increases and/or the partial pressure of CO is decreased.

## 2. Results and discussion

The olefin complexes [5] Pt(C<sub>7</sub>H<sub>10</sub>)<sub>3</sub>, (C<sub>7</sub>H<sub>10</sub> = norbornene), Pt<sub>2</sub>(dba)<sub>3</sub> · toluene and Pt(COD)<sub>2</sub> (COD = cyclooctadiene) were used for the reaction with carbon monoxide. Although the platinum(0) olefin complexes are stable in air in the solid state, they promptly react with carbon monoxide, both in solution and in the solid state. The reactions were followed by gasvolumetry: absorption in cyclohexane or toluene is fast, the rate of carbonylation of Pt<sub>2</sub>(dba)<sub>3</sub> · toluene being slightly lower, presumably due to the low solubility of the starting platinum complex. The CO uptake was found to approach the CO:Pt molar ratio of 2 (see Table 1) under appropriate conditions, namely at 1°C at atmospheric pressure of carbon monoxide.

The insoluble carbonylation product was separated by filtration, and dried in a stream of carbon monoxide in order to minimize the loss of coordinated CO. Norbornene was identified as the only species in the filtrate by <sup>13</sup>C-NMR spectroscopy and dba was recovered in a substantially quantitative yield as the co-product of the carbonylation of Pt<sub>2</sub>(dba)<sub>3</sub> · toluene. On the contrary, the filtrate of the carbonylation reaction of Pt(COD)<sub>2</sub> showed IR carbonyl stretchings at 2071, 2022 and 1999 cm<sup>-1</sup>, due to some unidentified soluble carbonyl derivatives of platinum(0), and contained the displaced olefin. Although these data could suggest the presence

of an equilibrium involving soluble platinum carbonyl complexes, no reaction was observed by treating the insoluble carbonylation product with an excess of COD.

The carbonyl stretching vibrations of the carbonyl–platinum(0) derivative (see Table 2) are, in the decreasing order of wavenumbers, to be assigned to terminal, bridging bidentate and bridging tridentate carbonyl groups. Terminal CO stretching vibrations, for a neutral platinum derivative, is expected to be slightly above  $2070\text{ cm}^{-1}$ , in agreement with our own results and with the spectroscopic studies of CO adsorbed on platinum metal [4, 10a,b]. The assignments of Table 2 concerning triply bridging carbonyl groups require some comments. Crystallographically established [10c–f] molecular complexes containing triply bridging CO's and aliphatic tertiary phosphines as additional ligands show carbonyl stretching vibrations between  $1750$  and  $1769\text{ cm}^{-1}$ . By taking into consideration that a tertiary phosphine should have a bathochromic effect on the carbonyl stretching vibration (e.g.  $\text{Pt}_2\text{Cl}_4(\text{CO})_2$  [9d] and  $\text{PtCl}_2(\text{CO})(\text{PPh}_3)$  [10g] absorb at  $2136$  and  $2110\text{ cm}^{-1}$ , respectively), a value of about  $1800\text{ cm}^{-1}$  is in order for a triply bridging carbonyl group on an unsubstituted platinum(0) cluster. On the other hand, a value of  $1810\text{ cm}^{-1}$  has been reported [10a,h,i] for triply bridging CO's on a Pt(111) surface.

As shown in Table 2, no triply bridging carbonyl bands are observed in the spectrum of the product obtained from  $\text{Pt}_2(\text{dba})_3 \cdot \text{toluene}$ . The different rate of formation of the platinum carbonyl compound probably plays a role in determining the structure of the product and the hapticity of the ligand. It is worth noting that no triply bridging carbonyl groups are present in Chini's anionic triangulo clusters [4]  $[\text{Pt}_3(\text{CO})_3(\mu_2\text{-CO})_3]_n^{2-}$ .

The carbonylated platinum samples are stable only under a carbon monoxide atmosphere at low temperature (around  $1^\circ\text{C}$ ). Products containing a CO:Pt molar ratio  $< 2$  were obtained by operating at temperatures higher than  $1^\circ\text{C}$  and/or by reducing the partial pressure of CO. Decarbonylation is not reversible; thus, the partially decarbonylated platinum-containing product

does not undergo carbon monoxide absorption at room temperature (r.t.) and atmospheric pressure. From the point of view of their thermal stability, our carbonyl derivatives appear to be less stable than the carbonylated product obtained by Booth, Chatt and Chini [2a,b]; a different structure is therefore suggested.

Starting from microcrystalline  $\text{Pt}(\text{C}_7\text{H}_{10})_3$ , the formation of  $[\text{Pt}(\text{CO})_2]_n$  was found to occur in the solid state, as revealed by X-ray diffraction. The product of carbonylation is amorphous. By heating at  $250^\circ\text{C}$ , CO was lost almost quantitatively and platinum metal was obtained, as identified by its powder X-ray pattern. The reflections were broad indicating small size of the metal particles. The formation of platinum metal from the intermediate carbonyl cluster was found to be endothermic; this is consistent with the thermodynamic data presently available on the formation of cluster carbonyl complexes from compounds of lower nuclearity, the process being entropy-driven [10j–l].

That the insoluble carbonylation product of platinum has a short-range ordered structure and is in a less stable situation than even finely divided platinum metal, is shown by its reactivity. In a second step of the carbonylation experiment with  $\text{Pt}(\text{C}_7\text{H}_{10})_3$  at  $1^\circ\text{C}$ , addition of a toluene solution of di-iodine saturated with carbon monoxide led to the substantially quantitative formation of  $\text{PtI}_2(\text{CO})_2$  as the only observable product [11]. This experiment could successfully be repeated with partially decarbonylated products. Quantitative evolution of coordinated carbon monoxide to give  $\text{Pt}(\text{dppe})_2$  was observed upon addition of bisdiphenylphosphinoethane.

This study has also established quite conclusively that the norbornene platinum(0) complex is thermodynamically unstable with respect to platinum metal. In fact, adding a catalytic amount of carbon monoxide to a solution of  $\text{Pt}(\text{C}_7\text{H}_{10})_3$  under dinitrogen causes the slow precipitation of platinum metal.

The reaction of  $\text{Pt}_2\text{dba}_3$  with carbon monoxide was reported to yield [8b] platinum nanoparticles with a cuboctahedral shape (TEM analysis), the cuboctahedron being a fragment of the cubic close packing of the metal. Several years ago Chini [3b] calculated that a two-layer cuboctahedron (55 metal atoms) has a surface which can accommodate 132 carbonyl groups (CO:Pt molar ratio of 2.4) at distances compatible with their van der Waals interactions, with  $1.5\text{ \AA}$  as the van der Waals radius of CO. By assuming that steric hindrance is the prevailing limiting factor, Chini concluded that a CO:Pt molar ratio of 2.4 is consistent with clusters of that size. Smaller or larger clusters could give rise to higher or lower CO:Pt molar ratios, respectively. On similar grounds, we have calculated the idealized CO:Pt molar ratios observable for cuboctahedral clusters covered by CO ligands, as a function of the size of the cuboctahedron, see Table 3. The Pt–Pt distance has

Table 2  
Carbonyl stretching vibrations of the carbonylation product (Nujol,  $\text{cm}^{-1}$ )

Starting material	Terminal CO	$\mu_2$ -CO	$\mu_3$ -CO
$\text{Pt}(\text{C}_7\text{H}_{10})_3$	2072	1898	1823
$\text{Pt}_2(\text{dba})_3 \cdot \text{toluene}$	2072	1889	
$\text{Pt}(\text{COD})_2$	2045	1882	1810
$\text{Pt}(\text{dba})_2^a$	2060	1885	
$\text{K}_2\text{PtCl}_4^b$	2068	1891	

<sup>a</sup> Ref. [8b].

<sup>b</sup> Ref. [2a].

Table 3  
CO:Pt molar ratio for different cuboctahedral clusters at full coverage of the surface<sup>a</sup>

$C_o$	$n_i$	$n_{cs}$	$n_{ex}$	$h_c$ (Å)	$A_s$ (Å <sup>2</sup> )	$n_{CO}$	CO:Pt
1	3	13	12	8.61	256	53	4.1
2	5	55	42	13.14	597	124	2.3
3	7	147	92	17.68	1080	225	1.5
4	9	309	162	22.21	1706	355	1.1

<sup>a</sup>  $C_o$ , number of cuboctahedral shells;  $n_i$ , number of close packed layers;  $n_{cs}$ , number of metal atoms forming the cluster;  $n_{ex}$ , number of external metal atoms in the cluster;  $h_c$ , height of the cuboctahedral surface available for CO binding. Height  $h_c$  corresponds to  $2.27(n_i - 1) + 2 d_{Pt-CO}$ ;  $A_s$ , cuboctahedron surface area,  $[3h_c^2(3 + \sqrt{3})/4]$ ;  $n_{CO}$ , number of CO ligands which can be packed in  $A_s$  on the hypothesis that the steric demand of each CO is  $4.8 \text{ \AA}^2$ ; CO:Pt molar ratio  $[n_{CO}/n_{cs}]$ .

been assumed to be the same as that in platinum metal ( $2.775 \text{ \AA}$ ); under this assumption, the close-packed layers ( $2 d_{Pt-Pt}/\sqrt{6}$ ) are separated by  $2.27 \text{ \AA}$ . For each cuboctahedron, the surface available to the carbonyl groups is a cuboctahedron of height defined by the appropriate number of metal layers added to twice the Pt–CO distance ( $2.04 \text{ \AA}$ ) [12], see Fig. 1. Table 3 has been prepared by assuming a steric demand for ligated carbon monoxide of  $4.8 \text{ \AA}^2$ , as calculated for the crowded iridium(0) cluster  $\text{Ir}_6(\text{CO})_{16}$  [13]. Thus, the experimental results are best accounted by a 55-atom cluster being the primary product of the reaction between the olefin platinum(0) complex and carbon monoxide. Useful comparison can be made with the platinum large clusters recently synthesized and crystallographically characterized by Ceriotti and coworkers [14].

In conclusion, this paper suggests that the stability of the olefin platinum(0) complexes is most likely due to the steric bulk of the ligands preventing the platinum atoms from approaching each other and form plat-

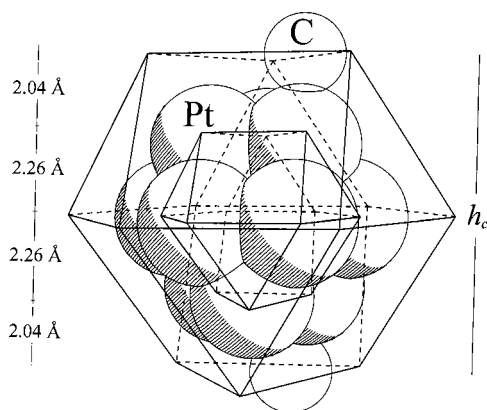


Fig. 1. Cuboctahedron cluster of 13 platinum atoms showing some of the parameters used in Table 3.

inum–platinum bonds. With the less hindered carbonyl groups, formation of small clusters is possible as a primary act towards the formation of larger clusters and finally of bulk metal. Last but not least, this paper definitely establishes that uncharged carbonyl derivatives of platinum(0) are unstable with respect to platinum metal. The remarkable reactivity of the carbonylation product towards both di-iodine and the bidentate phosphine suggests the possibility of using the carbonylation reaction of the platinum(0) olefin complexes for the preparation of highly reactive platinum.

### 3. Experimental

All preparations were carried out using standard Schlenk techniques. All 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. The compounds  $\text{Pt}(\text{C}_7\text{H}_{10})_3$  [5a,b],  $\text{Pt}(\text{COD})_2$  [5b],  $\text{Pt}_2\text{I}_4(\text{CO})_2$  [9d], and  $\text{PtI}_2(\text{CO})_2$ , as the predominant *trans*-isomer [9d] were synthesized as reported in the literature and found to correspond analytically and spectroscopically to the literature data. The dba complex  $\text{Pt}_2(\text{dba})_3$  was prepared according to the literature [5h] and then recrystallized from toluene to give the new solvated product  $\text{Pt}_2(\text{dba})_3 \cdot \text{toluene}$ . The platinum(0) olefin complexes are stable in air in the solid state; they react with dioxygen in solution. The dibenzylideneacetone complex  $\text{Pt}_2(\text{dba})_3 \cdot \text{toluene}$  has a limited solubility in organic solvents such as toluene, chloroform, acetone, and THF whereas  $\text{Pt}(\text{C}_7\text{H}_{10})_3$  and  $\text{Pt}(\text{COD})_2$  are very soluble even in hydrocarbon solvents. The molar extinction coefficient ( $\epsilon = 1962 \text{ l mol}^{-1} \text{ cm}^{-1}$ ) of the CO stretching vibration ( $2123 \text{ cm}^{-1}$ ) of *trans*- $\text{PtI}_2(\text{CO})_2$  was measured by using standardized toluene solutions under a carbon monoxide atmosphere to avoid dimerization to  $\text{Pt}_2\text{I}_4(\text{CO})_2$  [9d], the thickness of the cell ( $1.05 \times 10^{-2} \text{ cm}$ ) being determined by the interference method. Elemental analyses (C, H, N) were performed in the Laboratorio di Microanalisi della Facoltà di Farmacia, Università di Pisa, with a C. Erba mod. 1106 elemental analyzer. IR spectra were measured with an FT-IR Perkin-Elmer mod. 1725X spectrophotometer. The X-ray powder diagrams were measured with a Siemens D5000 diffractometer equipped with an environmental cell (Bühler HDK-2.4) for work under a controlled atmosphere: the platinum sample holder was protected with a corundum plate in order to avoid interference with the diffraction lines coming from the sample holder. Nuclear magnetic resonance solution spectra were recorded using a Varian Gemini 200 MHz instrument.

### 3.1. Reaction of $\text{Pt}(\text{C}_7\text{H}_{10})_3$ with CO

A cyclohexane solution (50 cm<sup>3</sup>) of  $\text{Pt}(\text{C}_7\text{H}_{10})_3$  (1.68 g, 3.52 mmol) was reacted with carbon monoxide; after about 5 min at r.t., a dark brown precipitate was obtained in a colourless solution. After decanting the solution off, the solid was washed with cyclohexane (3 × 50 cm<sup>3</sup>; norbornene was identified in the filtrate using <sup>13</sup>C-NMR spectroscopy) and dried under carbon monoxide (0.76 g; 86% yield calculated as  $\text{Pt}(\text{CO})_2$ ). IR (Nujol, cm<sup>-1</sup>): 2072, 1898, 1823. IR spectra of samples even briefly exposed to air showed loss of bridging carbonyls, and decreased intensity of the terminal carbonyls. X-ray powder diffraction showed this solid to be amorphous. Drying in vacuo, or even reducing the carbon monoxide pressure led to loss of bonded carbon monoxide. Products which had experienced partial decarbonylation did not absorb CO back again. Upon exposure to air, the product may glow.

A gasvolumetric experiment was carried out at 1°C with 0.080 g of  $\text{Pt}(\text{C}_7\text{H}_{10})_3$  (0.167 mmol) in 25 cm<sup>3</sup> of toluene, carbon monoxide was found to be absorbed corresponding to a CO:Pt molar ratio of 1.95 in about 25 min, 90% of the CO absorption being secured in the first 10 min. By adding 5.4 cm<sup>3</sup> of a toluene solution of di-iodine (0.17 g, 0.67 mmol) saturated with CO the dark precipitate was converted to the soluble  $\text{PtI}_2(\text{CO})_2$ , as shown by the IR spectrum of the decanted solution, with absorption bands at 2147 and 2123 cm<sup>-1</sup>. The measured IR absorbance of the CO stretching vibration at 2123 cm<sup>-1</sup> was  $A = 0.110$ , corresponding to 0.162 mmol of platinum, i.e. up to 97% of the initial platinum.

The CO uptake was also measured in toluene at 28.6°C. In a gasvolumetric experiment 0.125 g of  $\text{Pt}(\text{C}_7\text{H}_{10})_3$  (0.262 mmol) in 25 cm<sup>3</sup> of toluene absorbed 0.391 mmol of carbon monoxide for a CO:Pt molar ratio of 1.49. By sequentially adding 8.0 cm<sup>3</sup> of a toluene solution of di-iodine (0.25 g, 0.99 mmol) saturated with CO, an absorption of CO was measured (0.132 mmol, corresponding to an overall CO:Pt molar ratio of 2.0). The precipitate fell into solution, being converted to  $\text{PtI}_2(\text{CO})_2$  ( $\nu_{\text{CO}}$ ). The absorbance of the 2123 cm<sup>-1</sup> band of *trans*- $\text{PtI}_2(\text{CO})_2$  was  $A = 0.166$  corresponding to 0.266 mmol of platinum, i.e. to a substantially quantitative conversion of the initial platinum, within experimental error.

The carbonylated product, as recovered from a preparative reaction (LL-191; 0.123 g) carried out at r.t. and dried in a stream of carbon monoxide (at r.t.), was suspended in toluene (25 cm<sup>3</sup>) and stirred under carbon monoxide in a gasvolumetric apparatus at 28.6°C. No absorption of gas was observed. On the other hand, addition of 5.6 cm<sup>3</sup> of a toluene solution of di-iodine (0.17 g, 0.67 mmol) caused the absorption of 0.281 mmol of CO. On the basis of these data the minimal

formula of the starting material was calculated to be  $\text{Pt}(\text{CO})_{1.46}$ . The precipitate fell into solution, being converted into  $\text{PtI}_2(\text{CO})_2$  ( $\nu_{\text{CO}}$ ). The measured IR absorbance of the CO stretching of  $\text{PtI}_2(\text{CO})_2$  at 2123 cm<sup>-1</sup> was  $A = 0.369$  corresponding to 0.548 mmol of platinum.

A sample of platinum metal, obtained by heating the carbonylated product at 200°C in vacuo, did not react with I<sub>2</sub> under carbon monoxide in toluene; there was no CO uptake, and no CO bands were observed in the IR spectrum of the liquid phase.

A sample of  $\text{Pt}(\text{C}_7\text{H}_{10})_3$  (0.136 g, 0.28 mmol) was dissolved in C<sub>6</sub>D<sub>6</sub> in an NMR tube; the solution was frozen at liquid nitrogen temperature and briefly evacuated. A limited amount of carbon monoxide was then introduced and the NMR tube was flame sealed. By measuring the NMR spectra at r.t., only  $\text{Pt}(\text{C}_7\text{H}_{10})_3$  and a trace of free norbornene was initially observed; in 4 days the spectrum of norbornene and the presence of platinum metal were observed. No decomposition of  $\text{Pt}(\text{C}_7\text{H}_{10})_3$  was observed in a similar experiment carried out in the absence of carbon monoxide.

In a gasvolumetric experiment, 0.086 g of  $\text{Pt}(\text{C}_7\text{H}_{10})_3$  (0.180 mmol) in 25 cm<sup>3</sup> of toluene absorbed 8.7 cm<sup>3</sup> of carbon monoxide (0.343 mmol, CO:Pt = 1.90) at 25.0°C. By adding 9.3 cm<sup>3</sup> of a toluene solution of bisdiphenylphosphinoethane (0.33 g, 0.83 mmol) saturated with CO, an evolution of 0.296 mmol of CO was measured, corresponding to 86% of the expected amount. The resulting yellow solution revealed a <sup>31</sup>P-NMR spectrum with a resonance at 30.64 ppm  $J_{\text{Pt-P}} = 3730$  Hz, in agreement with the literature data for  $\text{Pt}(\text{dppe})_2$  [15].

### 3.2. X-ray powder diffractometry

The reaction of  $\text{Pt}(\text{C}_7\text{H}_{10})_3$  with carbon monoxide, which also occurs in the solid state, was followed in situ by time-resolved powder X-ray diffraction in an experiment carried out at 25°C. The pattern of crystalline  $\text{Pt}(\text{C}_7\text{H}_{10})_3$ , which was consistent with the calculated diagram of the known structure [5b], remained observable for about 60 min with unchanged position and relative intensity of the reflections; they progressively disappeared (within 3–4 h) leaving all intensity in the background, consistent with the formation of an amorphous product. In a thermogravimetric experiment, carried out under an atmosphere of carbon monoxide (gradient of temperature: 5°C min<sup>-1</sup>),  $\text{Pt}(\text{C}_7\text{H}_{10})_3$  reacted in two steps giving platinum metal, through  $\text{Pt}(\text{CO})_2$ . At 90°C the carbonylated product starts to decompose to platinum metal in an endothermic reaction. The product of carbonylation, upon heating at 250°C released carbon monoxide with a weight loss of 17% (22% expected for the formulation  $[\text{Pt}(\text{CO})_2]_n$ ); the decarbonylated product was found to display the X-ray powder diffraction pattern of bulk metal.

### 3.3. Reaction of $Pt(COD)_2$ with CO

A solution of the platinum derivative (0.055 g, 0.134 mmol) in cyclohexane (25 cm<sup>3</sup>) was treated quickly with carbon monoxide to yield a dark brown solid and a yellow solution. A gasvolumetric uptake of 5.9 cm<sup>3</sup> of carbon monoxide (0.216 mmol, CO:Pt = 1.61 at 20.6°C) was measured and found to substantially proceed to completion in about 10 min. After filtration and repeated washings the brown solid was dried under carbon monoxide. IR (nujol, cm<sup>-1</sup>): 2045, 1882, 1810. An IR spectrum of the filtrate showed carbonyl bands at 2071, 2022, 1999 cm<sup>-1</sup>, respectively. The carbonylated product does not react at r.t. with an excess of COD.

A sample of the carbonylated product was treated with 5 cm<sup>3</sup> of a toluene solution of di-iodine (0.11 g, 0.43 mmol) under carbon monoxide. An IR spectrum of the solution showed the bands of *cis*- and *trans*-PtI<sub>2</sub>(CO)<sub>2</sub>, in addition to a band at 2088 cm<sup>-1</sup> due to an unidentified product.

### 3.4. Reaction of $Pt_2(dba)_3 \cdot$ toluene with CO

A suspension of the platinum derivative (0.095 g, 0.159 mmol of platinum) in cyclohexane (25 cm<sup>3</sup>) was reacted with carbon monoxide. In about 2 h a dark brown solid and a yellow solution were obtained. The uptake of carbon monoxide corresponded to a CO:Pt molar ratio of 1.76 at 20°C: about 92% of the gas absorption was over within the first 50 min. In a preparative reaction, the dibenzylideneacetone complex (0.45 g, 0.759 mmol of platinum) in cyclohexane (100 cm<sup>3</sup>) was reacted with CO at atmospheric pressure for 2 days at r.t. The resulting solid was washed several times with cyclohexane, and dried under carbon monoxide (0.147 g, 77% yield as Pt(CO)<sub>2</sub>). IR (nujol, cm<sup>-1</sup>): 2072, 1889. The free ligand was recovered unchanged (IR comparison) from the filtrate in a 74% yield.

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