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# Surface-Mediated Organometallic Synthesis: Preparation of $[Pt_3(CO)_6]_n^{2-}$ ($n$ = 3, 4) by the Carbonylation of Platinum Complexes on MgO under CO and CO + $H_2$

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Treatment in CO or CO + $H_2$ of samples prepared by adsorption of $Pt(C_3H_5)_2$ on MgO leads to carbonylation reactions forming $[Pt_3(CO)_6]_n^{2-}$ ($n$ = 3, 4) on the MgO surface at room temperature. These anions can be extracted into solution by cation metathesis, giving efficient syntheses of the clusters. The surface-mediated synthesis can be directed to either anionic cluster. The reactivity is controlled by the basicity of the MgO surface and the gas environment. Similar surface organometallic chemistry takes place when the precursor is $Na_2PtCl_6{\cdot}6H_2O$, but higher temperatures (80 °C) are required and mixtures are not always avoidable. The organometallic chemistry on the basic MgO surface is similar to that occurring in basic solution, discovered by Longoni and Chini.

## Introduction

Reactivities of organometallic compounds on metal oxide surfaces are often similar to their reactivities in solutions that contain functional groups analogous to those present on the surface.[1,2] Most organometallic reactions on surfaces give complicated mixtures, but some can be controlled to give high yields of individual products. For example, the reductive carbonylation of mononuclear osmium[3] and ruthenium[4] complexes on the basic MgO surface gives osmium and ruthenium carbonyl cluster anions in high yields, and some of the surface-mediated syntheses are simpler and more efficient than the established solution procedures.[3]

The surface-mediated synthesis of metal carbonyl clusters can provide routes to compounds not accessible by conventional solution techniques. For example, $[Os_5C(CO)_{14}]^{2-}$ was formed from $[Os_3(CO)_{12}]$ on MgO,[3] $[HOs_3(CO)_{10}(OH)]$ has been extracted in high yield from similar clusters bonded to silica,[5] carbonyl anions of rhodium have been formed in zeolite cages,[6] and osmium carbonyl anions have been formed in the supercages of NaY zeolite made basic by treatment with $NaN_3$. The latter material is a selective and stable catalyst for CO hydrogenation.[7]

Here we report carbonylation of platinum complexes on MgO to give high yields of $[Pt_3(CO)_6]_n^{2-}$ ($n$ = 3, 4). The organoplatinum chemistry on the MgO surface mimics the reductive carbonylation chemistry in basic solutions reported by Longoni and Chini.[8]

## Experimental Section

**Methods and Materials.** All syntheses and sample transfers were conducted with exclusion of air and moisture on a double-manifold Schlenk line, in a Vacuum Atmospheres drybox, in a batch autoclave, or in a copper-lined stainless-steel tubular flow reactor. $H_2$ and CO were UHP grade (Matheson). The CO was passed through a trap to remove traces of iron carbonyl contaminants. Typical flow rates of the gaseous reagents were 10 mL/min. The solvents were dried and deoxygenated prior to use. Tetrahydrofuran (THF), pentane, hexane, and diethyl ether were dried over sodium benzophenone ketyl; acetone was dried over 4A molecular sieve. Mg turnings were washed with dilute HCl followed by scrupulous rinsing with deionized water, then dried and stored under nitrogen. Tetra-*n*-butylammonium bromide (Aldrich) was recrystallized from acetone/ether/hexane before use. Extraction of surface organometallic species was performed with a solution of the appropriate salt (e.g., tetra-*n*-butylammonium bromide) in acetone (0.02 M) or a suspension of the salt in THF. The MgO support (MCB-65-1 powder, MCB Reagents, surface area about 50 $m^2/g$) was calcined at 450 °C by heating in flowing $O_2$ (Matheson, extra dry grade) for 2 h, followed by evacuation for 12-14 h.

Infrared spectra were recorded with a Nicolet 7199 FTIR spectrometer with a spectral resolution of 4 $cm^{-1}$. Solution spectra were recorded with samples in a 0.2-mm $CaF_2$ or a 0.1-mm NaCl cell. Spectra of solids were recorded with samples in a controlled-atmosphere heatable flow cell.[9] X-ray fluorescence spectra of solid samples were recorded with a Philips 4100 spectrometer to determine the Pt contents.

**Preparation of Allylmagnesium Chloride.** The method was similar to that reported;[10] Mg turnings (0.974 g, 40.0 mmol) were placed in a 100-mL three-necked round-bottom flask containing a stirring bar and fitted with an adaptor for flow of nitrogen, a glass stopper, and a septum; the sample was degassed three or four times. Diethyl ether, freshly distilled (15 mL), was transferred into the flask by syringe. Iodine (0.104 g, 0.40 mmol) was added to the Mg under a blanket of nitrogen. The Mg and $I_2$ were stirred at room temperature until all the brown iodine color had disappeared. A solution of allyl chloride (0.40 mL, 0.38 g, 4.9 mmol) in 5 mL of diethyl ether was prepared in a degassed addition funnel. Under a rapid flow of nitrogen, the septum was removed from the round-bottom flask and the addition funnel attached. The flask was placed in an ethylene glycol/water bath cooled to −20 °C with liquid nitrogen. The temperature of the solution was maintained between −20 and −10 °C as the allyl chloride solution was added to the rapidly stirred Mg turnings over a period of 5 h. After all the $C_3H_5Cl$ had been added, the mixture was stirred for an additional hour at low temperature and then allowed to warm to room temperature over 30 min. The addition funnel was removed under a flow of nitrogen and replaced with a septum. The solution was then pumped to dryness, the Grignard reagent dissolved in 25 mL of ether, and the yield determined by acid quenching, followed by back titration with base. These results determined the amount of $PtCl_2$ to be used in the subsequent synthesis of the platinum allyl derivative.

**Preparation of Diallylplatinum.** A variation of the literature procedure[11] was followed. In a typical preparation, $PtCl_2$ (80 mg, 0.30 mmol) was partially dissolved in 5 mL of diethyl ether. An ether solution of allylmagnesium chloride, $7.0 \times 10^{-2}$ M (prepared from 0.97 g of Mg, 40 mmol, and 0.40 mL of allyl chloride, 0.38 g, 4.9 mmol, 56% yield as determined by acid-base titration) was placed in a dropping funnel. The mixture containing $PtCl_2$ was cooled to −78 °C in a dry ice bath, and the Grignard solution was added over a period of 5 h. The mixture was stirred at −78 °C for 20 h and then filtered at −20 °C. The ether was removed by evacuation at −20 °C and the residue extracted with pentane (30 mL) and filtered at −20 °C. The pentane was removed by evacuation at −20 °C, and the product was vacuum distilled, at room temperature, to a flask held at −40 °C. Colorless crystals, highly temperature sensitive, were collected. The product was identified by its IR spectrum (1261 s, 1099 ms, 1019 ms $cm^{-1}$).

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**Preparation of MgO-Supported Samples.** $[Pt(C_3H_5)_2]$ (precise weight unknown because of the volatility of sample) was dissolved in pentane with stirring, and MgO powder was added. The pentane was removed by evacuation at -20 °C, and the Pt content of the solid sample determined by X-ray fluorescence spectroscopy (3 wt %). The IR spectrum of the sample prepared from $[Pt(C_3H_5)_2]$ on MgO showed bands at 1260 m, 1020 s $cm^{-1}$.

$Na_2PtCl_6{\cdot}6H_2O$ (dissolved in deionized water) was deposited on MgO by the incipient wetness technique (just enough solution was used to fill the pores of the solid), and the solid was dried at 65 °C, under vacuum, for 12 h; the nominal Pt content was 1 wt %.

**Characterization of Surface Species by IR Spectroscopy.** Samples of the solid prepared from $[Pt(C_3H_5)_2]$ and MgO or from $Na_2PtCl_6{\cdot}6H_2O$ and MgO were pressed into thin self-supporting wafers and loaded into a controlled-atmosphere IR cell.[9] The flowing gas, CO or equimolar CO + $H_2$, was brought into contact with the wafer after thorough purging of the lines with He. IR spectra were recorded under controlled conditions (i.e., gas-phase composition, temperature). The temperature was raised in steps of 20–30 °C and maintained for 30 min after each change to allow equilibration.

**Extraction of Surface Species in a Controlled Atmosphere.** Experiments were performed with a glass apparatus designed to allow all the treatments, including extraction, to be carried out with the sample in a stabilizing environment of CO or CO + $H_2$. Experiments with samples prepared from $[Pt(C_3H_5)_2]$ and MgO were carried out as follows: A 50-mL round-bottom flask was fitted with a glass tube having a medium-porosity glass frit and topped with an adapter for introduction of gas (CO or equimolar CO + $H_2$) and acetone solvent. The apparatus was equipped with an exit tube for the gas and an adapter for withdrawal of liquid samples. A small (100–300 mg) sample of the MgO-supported platinum was placed atop the frit in the drybox. A stream of CO or CO + $H_2$ was allowed to flow through the frit. Changes in the color of the initially off-white solid sample were monitored visually. The species formed on the MgO surface were extracted (under an atmosphere of CO or CO + $H_2$) by addition of an acetone solution of *n*-$Bu_4NBr$. Subsequent addition of diethyl ether induced rapid precipitation of the extracted organometallic species. The solution was pumped to dryness and the residue washed with several portions of ether, under an inert atmosphere, and recrystallized from THF/ether/pentane.

## Results

**Carbonylation of a Sample Prepared from $[Pt(C_3H_5)_2]$ on MgO.** A powder sample prepared from $[Pt(C_3H_5)_2]$ on MgO was placed on a frit in a glass tube, and a stream of CO (1 atm) was allowed to flow through it at room temperature. After approximately 30 min, the solid took on a pale purple color. The CO flow was allowed to continue for an additional 2 h to ensure complete reaction. A solution of *n*-$Bu_4NBr$ in acetone was then introduced into the sample chamber. The solution effectively extracted the surface organometallic species, taking on a red-violet appearance, and slowly passed through the frit to a flask below. A sample of the solution was taken by syringe and characterized by IR spectroscopy. The spectrum is virtually identical with that of $[Pt_9(CO)_{18}]^{2-}$, first reported by Longoni and Chini[8] ($\nu_{CO}$ = 2031 s, 1842 m $cm^{-1}$).

The solution was allowed to stand, and additional bands appeared ($\nu_{CO}$, $cm^{-1}$) at 2048 w sh and 1867 w, attributed to the presence of $[Pt_{12}(CO)_{24}]^{2-}$.[8] These bands increased in intensity over time, with a concomitant decrease of those assigned to $[Pt_9(CO)_{18}]^{2-}$. Since the IR cell was not rigorously airtight, it is inferred that contamination by air led to the conversion of the nonaplatinum carbonyl anion into the dodecaplatinum derivative. The $Pt_{12}$ cluster is kinetically more stable than the $Pt_9$ cluster in the presence of oxygen, and no further change was detected after 30 min. However, when the cell was opened to the atmosphere, reaction occurred, and the solution took on a yellow-green appearance, indicating the presence of $[Pt_{15}(CO)_{30}]^{2-}$. The solution then gradually turned olive green, characteristic of $[Pt_{18}(CO)_{36}]^{2-}$, and finally it became grayish, suggesting formation of highly dispersed metallic Pt.

These results are consistent with the reported observations that the reactivity of $[Pt_3(CO)_6]_n^{2-}$ toward oxidizing agents increases with decreasing *n*, and that the dianions (*n* = 3, 2, 1) are highly sensitive to atmospheric oxygen, with which they react to form the corresponding *n* + 1 derivatives.[8] Thus, under the conditions described, the anionic cluster $[Pt_9(CO)_{18}]^{2-}$ is the most reduced organometallic species detected, and it can be obtained with high selectivity by the surface-mediated organometallic synthesis.

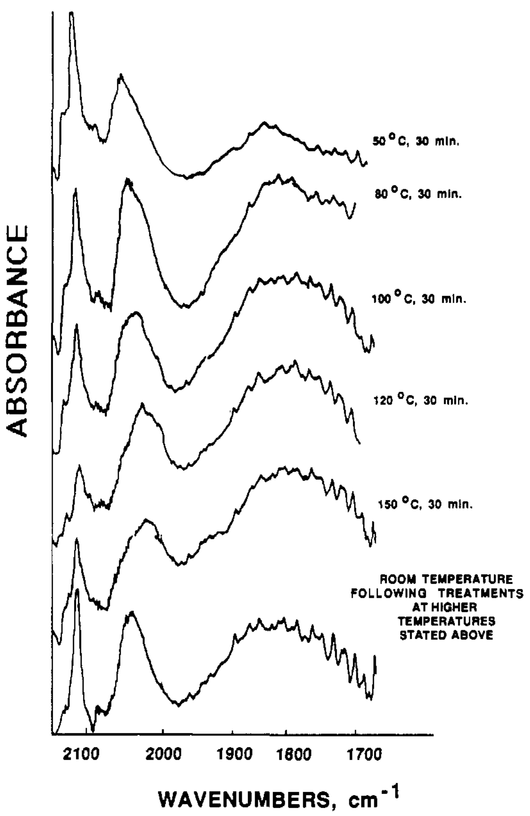

**Figure 1.** IR spectra of MgO-supported species formed from $[Pt(C_3H_5)_2]$ in the presence of CO at 1 atm.

The carbonylation of species formed from diallylplatinum on MgO was also monitored by in situ IR spectroscopy with the solid sample in the presence of flowing CO (1 atm). A few minutes after exposure to CO, at room temperature, the IR spectrum of the sample showed bands at 2046 s and 1846 m ($\nu_{CO}$, $cm^{-1}$), attributed to the presence of $[Pt_{12}(CO)_{24}]^{2-}$ on the surface. When the temperature was increased beyond 50 °C, broadening of the IR bands was observed, and a shift of the bridging CO band toward lower frequencies was observed (Figure 1), suggesting disproportionation, presumably via low-nuclearity Pt carbonyl intermediates, to form metallic Pt. Disappearance of all the carbonyl bands resulted when the sample was evacuated at 150 °C, suggesting the presence of metallic Pt particles.[12] The sample was gray after removal from the cell in the drybox. No extractable species were detected by IR spectroscopy when the sample was brought in contact with an acetone solution of *n*-$Bu_4NBr$.

The high-frequency band in the infrared spectrum, 2114 $cm^{-1}$ (Figure 1), is attributed to the presence of a carbonyl ligand terminally bound to an oxidized platinum center. This value agrees well with those found in the literature for carbon monoxide bound to oxidized platinum species.[13] The intensity of this high-frequency band decreased over time relative to the intensities of the

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bands characteristic of the platinum cluster, indicating the aggregation of surface platinum ions to form clusters. The increase of this band at higher temperatures, relative to the intensities of the bands of the carbonyl clusters, suggests decomposition of the clusters.

A similar in situ IR experiment was performed with an equimolar mixture of CO + $H_2$ instead of CO as the gas phase. Within minutes, at room temperature, the formation of Pt carbonyl species on the basic MgO surface was detected. However, the IR spectrum was more complex than that observed when the gas was just CO ($\nu_{CO}$ = 2048 vs, 1850 m, 1833 sh, 1816 sh $cm^{-1}$), and the bands were slightly shifted from the positions found for the sample formed under just CO. The IR spectrum of the sample under CO + $H_2$ is attributed to a mixture of $[Pt_{12}(CO)_{24}]^{2-}$ and $[Pt_9(CO)_{18}]^{2-}$, with the dodecaplatinum carbonyl cluster being the dominant species (estimated from the IR data to be *roughly* 70% of the metal carbonyl species). The presence of the $Pt_{12}$ carbonyl anion in a CO atmosphere and a mixture of this anion with the $Pt_9$ carbonyl anion in an atmosphere of CO/$H_2$ is attributed to the reduction of the former in $H_2$:[14]

$$3[Pt_{12}(CO)_{24}]^{2-} + H_2 \rightarrow 4[Pt_9(CO)_{18}]^{2-} + 2H^+ \quad (1)$$

After evacuation, the solid was gray, and no organometallic species could be extracted with an acetone solution of *n*-$Bu_4NBr$, consistent with disproportionation of carbonyl species in the absence of the stabilizing CO atmosphere and formation of metallic Pt on the MgO surface.

The difference in the results obtained in the in situ IR experiments and in the carbonylation experiments carried out with the sample on a frit in a glass tube, attached to a Schlenk line, is attributed to the sensitivity of the surface species to oxygen and our inability to exclude oxygen fully from the system used for the in situ IR experiments.

In an attempt to confirm that the presence of the dominant species on the surface (i.e., $[Pt_{12}(CO)_{24}]^{2-}$ or $[Pt_9(CO)_{18}]^{2-}$) was related to this critical difference in two types of apparatus, an experiment was performed by placing a sample of MgO-supported $[Pt(C_3H_5)_2]$ on a frit in a glass tube. This system was connected to the gas transport lines used for the in situ IR experiments. A stream of equimolar CO + $H_2$ was then allowed to flow through the sample at room temperature. Within 10 min, the color changed from the very light brown characteristic of the freshly supported species to blue-green, indicating the presence of $[Pt_{12}(CO)_{24}]^{2-}$ on the surface. After 30 min of reaction with flowing CO + $H_2$, the surface species was extracted with an excess of *n*-$Bu_4NBr$ in acetone. The IR spectrum of the extract solution was essentially the same as that obtained in the experiment carried out in the IR cell with CO + $H_2$. $[Pt_{12}(CO)_{24}]^{2-}$ ($\nu_{CO}$ = 2048 vs, 1861 s $cm^{-1}$) was the dominant organometallic species extracted from the surface, and the extraction experiment allowed detection of both terminal and bridging CO bands of the $[Pt_9(CO)_{18}]^{2-}$ derivative (*roughly* 30% of the organometallic species) (2033 sh, 1845 mw $cm^{-1}$). The IR spectrum was time dependent; the initially blue-green solution became red-violet on standing for ca. 30 min to yield $[Pt_9(CO)_{18}]^{2-}$ as the only carbonyl-containing species detected in solution.

This latter observation can be attributed to the presence of $H_2$ and/or trace amounts of water introduced with the solvent upon extraction. The reduction of the dodecaplatinum carbonyl derivative is effectively performed by either $H_2$ or water.[14b,c] Moreover, in the presence of $H_2$, the process is enhanced by trace amounts of water:[8]

$$3[Pt_{12}(CO)_{24}]^{2-} + H_2 + 2H_2O \rightleftarrows 4[Pt_9(CO)_{18}]^{2-} + 2H_3O^+ \quad (2)$$

In summary, the carbonylation of $[Pt(C_3H_5)_2]$ supported on MgO takes place under mild conditions (25 °C, 1 atm). Careful exclusion of oxygen from the reaction system allowed isolation and characterization of $[Pt_9(CO)_{18}]^{2-}$ as the predominant organometallic species on the surface. The IR spectra recorded in situ, on the other hand, showed that $Pt_{12}$ was the predominant organometallic species on the surface (Figure 1), and its presence is associated with the presence of small amounts of oxygen. As the temperature was raised beyond 50 °C, there was a disproportionation leading to the formation of metallic Pt.

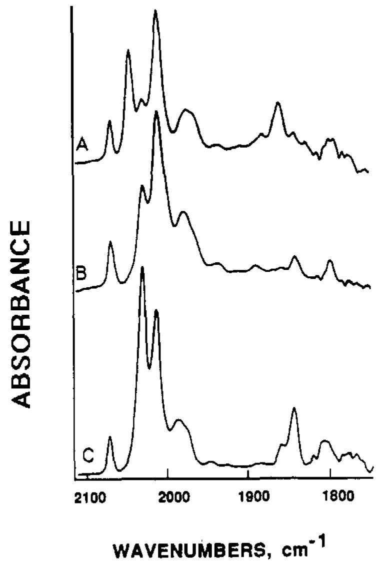

**Figure 2.** IR spectra of MgO-supported species formed from $Na_2PtCl_6{\cdot}6H_2O$ in the presence of CO or equimolar CO + $H_2$ (14 atm) and extracted into solution with *n*-$Bu_4NCl$ in acetone: (A) spectrum of sample heated in CO immediately following extraction; (B) spectrum of solution immediately following second extraction of the solid in the same way; (C) spectrum of sample heated in CO + $H_2$ immediately following extraction in the same way.

**Carbonylation of Sample Prepared from $Na_2PtCl_6{\cdot}6H_2O$ on MgO.** $Na_2PtCl_6{\cdot}6H_2O$ was brought in contact with MgO powder and the solid placed in an autoclave (or a copper-lined stainless-steel high-pressure tubular flow reactor), charged with CO ($P_{CO}$ = 14 atm) and held for 3 h at 80 °C. After cooling of the reactor to room temperature, the pressure was released and the autoclave (or tubular flow reactor) opened in the drybox. A dark green solid was observed. Extraction of the surface species was carried out with an acetone solution of *n*-$Bu_4NCl$, to form a dark-green solution, and the IR spectrum was immediately recorded ($\nu_{CO}$ = 2071 w, 2048 s, 2030 s, 2012 s, 1977 m br, 1967 sh, 1862 m, 1799 w br $cm^{-1}$) (Figure 2A). The bands at 2048 and 1862 $cm^{-1}$ are attributed to $[Pt_{12}(CO)_{24}]^{2-}$, and the band at 2030 $cm^{-1}$ is attributed to $[Pt_9(CO)_{18}]^{2-}$. The bands at 2071, 2012, 1977, 1967, and 1799 $cm^{-1}$ are attributed to a species designated as **1**. The $Pt_{12}$ and $Pt_9$ species were identified by comparison with the IR spectra of authentic samples.[8] The solid was subsequently stirred with a second aliquot of *n*-$Bu_4NCl$ to form, after filtration, a red-violet solution, and the IR spectrum was recorded immediately ($\nu_{CO}$ = 2071 m, 2030 m s, 2012 s, 1977 m br, 1967 sh, 1840 w, 1977 w $cm^{-1}$) (Figure 2B). The bands at 2030 and 1840 $cm^{-1}$ are attributed to $[Pt_9(CO)_{18}]^{2-}$; the remaining bands are assigned to **1**.

The IR spectrum of the extracted species changed with time, even with the sample under nitrogen. The initially green solution became red-violet within a few minutes of the extraction in the drybox; the changes were monitored by IR spectroscopy. Disappearance of the bands assigned to the $Pt_{12}$ cluster and **1** was observed to yield $[Pt_9(CO)_{18}]^{2-}$ as the only organometallic species detected in solution. Attempts to quench the redox reaction by rapid filtration after addition of *n*-$Bu_4NCl$ in acetone failed, indicating that interactions between species in solution were responsible for the changes observed.

Similar results were obtained when the reaction was carried out with a mixture of CO + $H_2$ as the gas phase. In this experiment, the reductive carbonylation of $Na_2PtCl_6{\cdot}6H_2O$ on MgO

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[14] (a) See ref 8. (b) Bhaduri, S.; Sharma, K. R. *J. Chem. Soc., Chem. Commun.* **1983**, 1412. (c) Basu, A.; Bhaduri, S.; Sharma, K. R. *J. Chem. Soc., Dalton Trans.* **1984**, 2315.

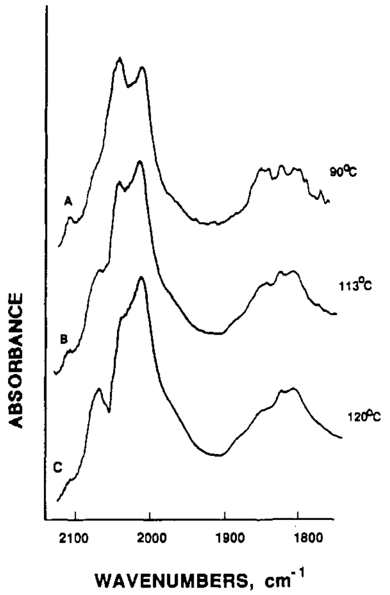

**Figure 3.** IR spectra of MgO-supported species formed from $Na_2PtCl_6 \cdot 6H_2O$ in the presence of CO at 1 atm.

was carried out with an equimolar mixture of CO + $H_2$ (P = 14 atm). The reaction was performed in an autoclave at 80 °C. On unloading, the sample was green, suggesting the presence of the $Pt_{12}$ cluster on the surface.[15] However, extraction of the surface species with *n*-$Bu_4NBr$ in acetone gave a red-violet solution. The IR spectrum of the solution, obtained immediately after the extraction, showed the presence of $[Pt_9(CO)_{18}]^{2-}$ ($\nu_{CO}$ = 2030 vs, 1840 m cm$^{-1}$) and **1** in roughly equal amounts (Figure 3C). These observations suggest the relatively rapid reduction of the $Pt_{12}$ carbonyl dianion upon extraction in the presence of the $H_2$, and they contrast with the observations made when the reaction was carried out with CO as the gas phase, when the $Pt_{12}$ derivative was detected by IR spectroscopy shortly after extraction. A seemingly similar facile redox behavior has been observed during the contacting of the $Pt_9$ carbonyl dianion with a $SiO_2$ surface.[16]

Analysis of the extracted surface species obtained from a number of experiments carried out under different CO partial pressures (e.g., $P_{CO}$ = 10–15 atm) revealed that although the relative amounts of $[Pt_{12}(CO)_{24}]^{2-}$, $[Pt_9(CO)_{18}]^{2-}$, and **1** varied slightly with reaction conditions, the intensities of the bands assigned to **1** remained essentially in the same proportions. Further, as the transformations took place in the solution on standing, the spectra showed that, as **1** disappeared, the relative intensities of the IR bands assigned to this species remained essentially unchanged.

Attempts to detect a solvent effect were carried out by performing the extraction with a THF suspension of *n*-$Bu_4NCl$ (or PPNCl). However, the extraction was inefficient, probably because the solubility of *n*-$Bu_4NCl$ (or PPNCl) in THF is low, thus requiring relatively long contact times, approximately 15 min. The IR spectra obtained were similar to those recorded after extraction with acetone.

The reductive carbonylation of $Na_2PtCl_6 \cdot 6H_2O$ on the basic MgO support was also monitored by in situ IR spectroscopy under CO flow ($P_{CO}$ = 1 atm). The temperature was increased in intervals of 30 °C and maintained for 30 min before the spectrum was recorded. The spectrum obtained at 90 °C showed the bands characteristic of linear and bridging CO ligands in $[Pt_{12}(CO)_{24}]^{2-}$, and also **1** ($\nu_{CO}$ = 2046 s br, 2014 s br, 1830 m br cm$^{-1}$) (Figure 3A). However, the presence of the $Pt_9$ derivative could not be inferred because of the broadness of the bands characteristic of the solid sample. The spectrum obtained at 113 °C includes a band at 2068 m sh cm$^{-1}$ (characteristic of linear CO chemisorbed on metallic Pt[12]) that grew in with a concomitant decrease of the bands assigned to the molecular surface species; the band attributed to bridging CO groups also broadened and shifted to lower frequency (Figure 3B). When the temperature was increased to 120 °C, sharpening of the bands characteristic of linear and bridging CO chemisorbed on Pt particles was observed ($\nu_{CO}$ = 2070 m, 1853 sh cm$^{-1}$) (Figure 3C). The bands at 2013 and 1807 cm$^{-1}$ are assigned to linear and bridging CO adsorbed on metallic Pt atoms interacting with negatively charged framework oxygen atoms.[17] When the sample was removed from the cell in the drybox, it was dark gray. No extractable species could be obtained with a solution of *n*-$Bu_4NCl$ in acetone. These results are consistent with the presence of metallic Pt.

In an attempt to increase the thermal stability of the molecular species formed on the basic MgO support, a reaction was carried at high CO partial pressures in the flow reactor. The molecular species on the surface were formed by passing CO at 14 atm and 80 °C for 3 h. Subsequently, the CO partial pressure was increased gradually to 44 atm, and the temperature was held at 150 °C for 2 h. When the sample was removed from the reactor in the drybox, it was dark gray. No extractable species could be detected by IR spectroscopy. Evidently metal particles had again formed.

In summary, these results show that the use of $Na_2PtCl_6 \cdot 6H_2O$ as a precursor leads, after reductive carbonylation, to formation of $[Pt_{12}(CO)_{24}]^{2-}$ as the predominant organometallic species on the MgO surface. However, a reductive disproportionation reaction occurs upon extraction to form the nonaplatinum cluster anion, at the expense of the dodecaplatinum anion and **1**. Further, the material turns gray, indicating the presence of Pt in the metallic form. Hydrogen evidently facilitates the redox process, forming Pt and the more highly reduced $[Pt_9(CO)_{18}]^{2-}$.

## Discussion

The chemistry of the platinum carbonyls formed from $[Pt(C_3H_5)_2]$ on the basic MgO surface in the absence of water is relatively straightforward and easily controlled, giving $[Pt_9(CO)_{18}]^{2-}$, which can be extracted in high yield. The pattern of reactivity with $O_2$, $H_2$, and CO is consistent with the solution chemistry.

The chemistry of the platinum carbonyls formed from aqueous $Na_2PtCl_6 \cdot 6H_2O$ on the MgO surface (carried out at 80 °C) is more complicated and inferred to be influenced by water. This chemistry is not fully characterized; the product **1** is not identified. The observation that all the bands in the IR spectrum attributed to **1** disappeared in unison during reaction suggests that **1** may be tentatively assigned as a single compound. Thus, **1** may be a product of the interaction of the $Pt_{12}$ carbonyl anion and the $Pt_9$ carbonyl anion formed on the MgO surface, since these two species are known to react under relatively mild conditions.[19] This suggestion would explain the absence of **1** on the surface or in solution (after extraction of the surface species) when the $Pt(allyl)_2$ derivative was used as the precursor, since reductive carbonylation in this case was performed at room temperature.

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(15) Additional evidence for the presence of the $Pt_{12}$ cluster on the surface was obtained by in situ IR spectroscopy, with an equimolar mixture of CO + $H_2$ (P = 1 atm) as the gas phase.

(16) When $[Pt_9(CO)_{18}]^{2-}$ in THF was brought in contact with silica, the red-violet solution changed color immediately to form a green compound on the support (Simpson, A. F.; Whyman, R. *J. Organomet. Chem.* **1981**, *213*, 157).

(17) The strong $Pt^0$–$O^{2-}$ interaction enhances $d\pi$–$p\pi^*$ back-donation from the Pt atom to the CO molecule, thus leading to a decrease in $\nu_{CO}$ greater than that observed when CO is adsorbed on a Pt atom of a particle. The interaction of some Pt atoms of a particle with adjacent and negatively charged framework oxygen atoms has been proposed for Pt-exchanged zeolites. Reduction of the metal was followed by CO chemisorption; the shift of the linear and bridged CO bands toward lower frequency was found to parallel the zeolite basicity.[18]

(18) de Mallmann, A.; Barthomeuf, D. In *Zeolites as Catalysts, Sorbents and Detergent Builders*; Karge, H. G., Weitkamp, J., Eds.; Elsevier: Amsterdam, 1989.

(19) The reactivity of $[Pt_{12}(CO)_{24}]^{2-}$ with $[Pt_9(CO)_{18}]^{2-}$ in refluxing acetonitrile is well documented; see, for example: (a) Washecheck, D. PhD Thesis, University of Wisconsin, 1980. (b) Washecheck, D. M.; Wucherer, E. J.; Dahl, L. F.; Ceriotti, A.; Longoni, G.; Manassero, M.; Sansoni, M.; Chini, P. *J. Am. Chem. Soc.* **1979**, *101*, 6112.

The redox behavior observed in solution upon extraction (i.e., conversion of the $Pt_{12}$ cluster anion to the $Pt_9$ cluster anion) may be associated with water introduced in the impregnation step, which was followed by mild drying. Reduction of the cluster might be accompanied by oxidation of CO, presumably by nucleophilic attack of water on coordinated CO groups to form $CO_2$ and $H^+$; the $CO_2$ that was presumably formed could be accounted for by a slight, undetectable decomposition of the Pt cluster.

The nature of the Pt carbonyl clusters present in solution reflects a competition between reduction by water and the reverse oxidation that can take place as a consequence of the increased acidity of the solution.

Reduction by water could also proceed as follows:[14]

$$3[Pt_{12}(CO)_{24}]^{2-} + H_2O \rightarrow 4[Pt_9(CO)_{18}]^{2-} + 2H^+ + \tfrac{1}{2}O_2 \quad (3)$$

Thus, wetting of the acetone with water from the impregnation step would account for the continued reaction observed after filtration. The halide-induced disproportionation of the $Pt_{12}$ carbonyl anion has also been suggested.[20]

Alternatively, the IR spectra assigned to **1** may be attributed to a mixture of compounds converted at comparable rates with the main component being $[Pt_6(CO)_{12}]^{2-}$ ($\nu_{CO}$ = 2012 cm$^{-1}$). Thus Figure 2A may be explained in terms of a redox system in which the main compounds are $[Pt_{12}(CO)_{24}]^{2-}$ ($\nu_{CO}$ = 2048, 1862 cm$^{-1}$), $[Pt_9(CO)_{18}]^{2-}$ ($\nu_{CO}$ = 2030, 1799 cm$^{-1}$), and $[Pt_6(CO)_{12}]^{2-}$ ($\nu_{CO}$ = 2012 cm$^{-1}$). Under these conditions, disappearance of the dodecaplatinum cluster is expected as a result of the well-documented[8] redox reaction between nonconsecutive Pt carbonyl clusters:[21]

$$[Pt_{12}(CO)_{24}]^{2-} + [Pt_6(CO)_{12}]^{2-} \rightarrow 2[Pt_9(CO)_{18}]^{2-} \quad (4)$$

Although the observed redox behavior may involve **1**, this compound was not detected (either on the surface or in solution, after extraction of the surface species) when the Pt(allyl)$_2$ derivative was used as the precursor. The kinetic instability of the $Pt_{12}$ derivative, prepared by the surface-mediated synthesis, is contrasted with the kinetic stability of the same compound obtained by the solution procedure.[8]

The transformations observed upon extraction of the surface species are enhanced in the presence of $H_2$ and do not appear to be related to the nature of the precursor on the MgO surface.

## Conclusions

The MgO surface can be used effectively as a medium for the carbonylation of Pt complexes under mild conditions, with the resulting anionic carbonyl clusters being stabilized by the basic support in the presence of CO. The transformations observed parallel the reductive carbonylation of the $Pt^{IV}$ species in basic solution.[8] The dominant species formed on the surface depend on the nature of the Pt precursor and are controlled by the reductive character of the gas phase.

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[20] One reviewer indicated (on the basis of his own observations) that the halide-induced disproportionation of $[Pt_{12}(CO)_{24}]^{2-}$

$$10[Pt_{12}(CO)_{24}]^{2-} + 9Cl^- \rightarrow 13[Pt_9(CO)_{18}]^{2-} + 3[Pt(CO)Cl_3]^-$$

takes place in methanol, acetone, or THF solutions containing moderate concentrations (0.01–0.1 M) of $Cl^-$. However, the presence of the mononuclear carbonyl anion was not detected in our extraction experiments.

[21] The weaker bands at 2071, 1977, and 2067 cm$^{-1}$ are not assigned. The presence of the band attributed to $[Pt_6(CO)_{12}]^{2-}$ ($\nu_{CO}$ = 2012 cm$^{-1}$) at higher frequency than that reported ($\nu_{CO}$ = 1995 cm$^{-1}$) may be associated with the transient nature of the experiment.

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# Matrix Isolation Spectroscopic Studies of Hydrogen-Bonded Complexes of Titanocene Dihalides with HCl

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The matrix isolation technique has been combined with infrared spectroscopy to characterize the interaction between $Cp_2TiF_2$ and $Cp_2TiCl_2$, and HCl. Isolated 1/1 complexes were observed for each pair of reactants; the $Cp_2TiF_2{\cdot}HCl$ complex was characterized by a red shift of the HCl stretching mode to 2440 cm$^{-1}$ and a dramatic broadening of this absorption. In addition, strongly perturbed Ti–F stretching modes were observed near 536 and 556 cm$^{-1}$. The spectral data collectively indicate formation of hydrogen-bonded complexes, from the HCl subunit to both of the halogens on the titanocene dihalide in a bidentate structure.

## Introduction

Transition-metal centers serve as Lewis acids, accepting electron density from the ligand or Lewis base during complex formation. On the other hand, ligands attached to metal centers can exhibit basic character and undergo acid catalyzed reactions. An important example of this is the acid-catalyzed hydrolysis of transition-metal halides; for example, the rate of hydrolysis of [*trans*-Co(en)$_2$F$_2$]$^+$ shows a distinct hydrogen ion dependence.[1,2] Also, the formation of adducts between transition-metal halides and strong Lewis acids points to the basic character of the metal halide.[3,4] Several studies have examined the Lewis acid chemistry of titanocene difluoride, $Cp_2TiF_2$, and presented evidence for complex formation.[4–6] In the most recent study, evidence was obtained for a hydrogen-bonded complex between $Cp_2TiF_2$ and 4-chlorophenol in chloroform from NMR and IR spectra.[6] Unfortunately, the infrared data consisted of only a single band, the O–H stretching mode, due to spectral limitations.

Related studies[7a–d] have been carried out by Lokshin and coworkers in which they examined the interaction of perfluorobutanol and HCl with a range of transition-metal carbonyls in liquid-xenon

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