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Surface-Mediated Organometallic Synthesis: The Role of the Oxidation State and of Ancillary Ligands in the High-Yield and Selective Syntheses of Platinum Carbonyl Dianions $[Pt_3(CO)_6]_n^{2-}$ ($n = 6, 5, 4, 3$) by Reductive Carbonylation under Mild Conditions and in the Presence of Surface Basicity of Various Silica-Supported Pt(IV) or Pt(II) Compounds

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The reductive carbonylation under 1 atm of CO and in the presence of surface basicity of silica-supported $Na_2[PtCl_6]$, $K_2[PtCl_4]$, $[Pt(CH_3CN)_2Cl_2]$, or $[Pt(COD)Cl_2]$ (COD = *cis*,*cis*-1,5-cyclooctadiene) leads to the formation in high yields of platinum carbonyl dianionic clusters $[Pt_3(CO)_6]_n^{2-}$ ($n = 6, 5, 4, 3$). Remarkably the silica surface plays a *key role* in these reductive carbonylations since no carbonyl cluster is obtained by reductive carbonylation of solid $Na_2[PtCl_6]$ in the absence of silica. The selectivity of the reaction can be easily tuned by controlling the surface metal loading, the basicity of the surface, and the nature of the platinum precursor (platinum oxidation state and nature of the coordination sphere). In particular, the one-step silica-mediated synthesis of $[Pt_{18}(CO)_{36}]^{2-}$ from $K_2[PtCl_4]$ (90% yield) is very convenient when compared to the traditional synthesis in methanol solution (67% yield), which requires two steps: (i) formation of $[Pt_{12}(CO)_{24}]^{2-}$ and (ii) addition of $Na_2[PtCl_6]$ drop by drop (molar ratio $[Pt_{12}(CO)_{24}]^{2-}$:$Na_2[PtCl_6]$ = 1:1) under a flow of CO.

Introduction

In the last 15 years surface-mediated synthesis of metal carbonyl clusters, whereby the surface of an inorganic oxide plays the role of the solvent in conventional syntheses, has grown as an attractive preparative method.[1−14] The variables that influence the yields and selectivity of surface reactions are numerous, for example, loading and specificity of the metal salt or organometallic precursor adsorbed on the surface of the oxide, chemical properties of the surface, nature of the gas atmosphere, temperature, and pressure. The reaction products are easily isolated by solvent extraction or sublimation. Very often, yields and selectivities are so high and reaction conditions so mild that surface-mediated organometallic syntheses can be recommended over traditional syntheses in solution.[13] Sometimes surface reactions are so much more selective than those carried out in solution that it was possible to obtain products that in solution have never been isolated, for example, $[Ru_3(CO)_{10}Cl_2]$.[9]

As a general trend, a strongly basic surface, such as MgO, favors the formation of anionic metal carbonyl clusters[1,4−6] while neutral carbonyl clusters are obtained on the surface of a rather neutral oxide such as silica.[2,3,10] In the last years some of us reported the syntheses of various neutral and anionic osmium,[7,8,14] ruthenium,[9] iridium,[11] and rhodium[12] clusters in high yields and with excellent selectivity by controlled reduction, in the presence of alkali carbonates on the surface, of silica-supported metallic salts or organometallic precursors. Addition of a relatively weak base not only favors removal of chloro ligands but produces an unexpected very high basicity of the silica surface, allowing the synthesis of anionic metal carbonyl clusters, which usually require in solution the use of hyperbasic conditions.[13] In this work we extended this new method of syntheses to platinum carbonyl clusters $[Pt_3(CO)_6]_n^{2-}$ ($n = 6, 5, 4, 3$) working at room temperature and under 1 atm of CO and starting from $Na_2[PtCl_6]$, $K_2[PtCl_4]$, $[Pt(CH_3CN)_2Cl_2]$, or $[Pt(COD)Cl_2]$ supported on a silica surface of different basicity by addition of CH_3CO_2Na, NaOH, or K_2CO_3. This family of carbonyl clusters, first synthesized in solution and fully char-

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Table 1. Synthesis of $[Pt_3(CO)_6]_n^{2-}$ (n = 6, 5, 4, 3) by Controlled Reduction of Silica-Supported $Na_2[PtCl_6]$, $K_2[PtCl_4]$, $[Pt(CH_3CN)_2Cl_2]$, or $[Pt(COD)Cl_2]$ in the Presence of Various Bases

starting material	metal loading Pt/silica	base	molar ratio Pt:Na or K	product	yield
$Na_2[PtCl_6]$	no silica	CH_3CO_2Na	1:10−30	no carbonyl species	
$Na_2[PtCl_6]$	3% Pt/silica	CH_3CO_2Na	1:30	$[Pt_{12}(CO)_{24}]^{2-}$	63%
$Na_2[PtCl_6]$	3% Pt/silica	CH_3CO_2Na	1:40	$[Pt_{12}(CO)_{24}]^{2-}$	70%
$Na_2[PtCl_6]$	3% Pt/silica	NaOH	1:10	$[Pt_{12}(CO)_{24}]^{2-}$	63%
$Na_2[PtCl_6]$	3% Pt/silica	NaOH	1:20	$[Pt_{12}(CO)_{24}]^{2-}$	18%
$Na_2[PtCl_6]$	30% Pt/silica	CH_3CO_2Na	1:20	$[Pt_{15}(CO)_{30}]^{2-}$	72%
$Na_2[PtCl_6]$	30% Pt/silica	CH_3CO_2Na	1:40	$[Pt_{15}(CO)_{30}]^{2-}$	73%
$K_2[PtCl_4]$	3% Pt/silica	CH_3CO_2Na	1:3	$[Pt_{18}(CO)_{36}]^{2-}$	90%
$K_2[PtCl_4]$	3% Pt/silica	CH_3CO_2Na[a]	1:10	$[Pt_{15}(CO)_{30}]^{2-}$	74%
$K_2[PtCl_4]$	3% Pt/silica	CH_3CO_2Na	1:40	$[Pt_{15}(CO)_{30}]^{2-}$	74%
$[Pt(CH_3CN)_2Cl_2]$	3% Pt/silica	NaOH	1:10	$[Pt_9(CO)_{18}]^{2-}$	20−25%
$[Pt(CH_3CN)_2Cl_2]$	3% Pt/silica	K_2CO_3	1.40	$[Pt_9(CO)_{18}]^{2-}$	20−25%
$[Pt(COD)Cl_2]$	3% Pt/silica	NaOH	1:10	$[Pt_{12}(CO)_{24}]^{2-}$	95%
$[Pt(COD)Cl_2]$	3% Pt/silica	K_2CO_3	1.40	$[Pt_9(CO)_{18}]^{2-}$	60%

[a] Use of NaOH instead of CH_3CO_2Na affords a mixture of $[Pt_{12}(CO)_{24}]^{2-}$ and $[Pt_9(CO)_{18}]^{2-}$ (ca. 14% and 6% yields, respectively).

acterized by Longoni and Chini in the late 1970s,[15] is of particular interest. For example, they can generate small platinum particles supported on inorganic oxides acting as precursors of catalysts with increased properties.[16−20]

Results and Discussion

Reductive Carbonylation of Silica-Supported $Na_2[PtCl_6]$ in the Presence of Various Bases. When a slurry of silica, $Na_2[PtCl_6]$ (3 wt % Pt with respect to silica), and CH_3CO_2Na (molar ratio Pt:Na = 1:5 or 1:10), dissolved in the proper amount of water, is stirred overnight at room temperature, evaporated to dryness, and exposed to CO at atmospheric pressure for 48 h in a closed reaction cylindrical Pyrex vessel, originally described for the reductive carbonylation of silica-supported rhodium and iridium chlorides,[3] a mixture of anionic platinum carbonyl clusters is generated. Extraction of the silica powder with degassed methanol, followed by addition of [PPN]-Cl (bis(triphenylphosphoranylidene)ammomium chloride) to the solution, leads to the precipitation of $[PPN]_2[Pt_{12}(CO)_{24}]$ along with small amounts of $[PPN]_2[Pt_{15}(CO)_{30}]$, as confirmed by IR spectroscopy (THF solution, ν_{CO} = 2043 (vs), 1862 (s) cm^{-1} and ν_{CO} = 2055 (vs), 1873 (s) cm^{-1} for $[Pt_{12}(CO)_{24}]^{2-}$ and $[Pt_{15}(CO)_{30}]^{2-}$, respectively). By working under the same conditions but using a higher amount of CH_3CO_2Na (molar ratio Pt:Na = 1:30 or 1:40), only the pure cluster $[PPN]_2[Pt_{12}(CO)_{24}]$ is obtained (63−70% yields; see Table 1 and Scheme 1). Therefore, an increase of the surface basicity leads to a decrease of the carbonyl cluster nuclearity, as reported to occur when working in solution.[15] Attempts to generate a lower nuclearity platinum carbonyl cluster by working under the same reaction conditions but in the presence of a stronger base such as NaOH failed, since the $[PPN]_2[Pt_{12}(CO)_{24}]$ cluster was always obtained (63% and 18% yield by using a molar ratio Pt:Na = 1:10 and 1:20, respectively). It appears that a too high surface basicity affords only relatively low yields of carbonyl clusters, as previously observed for the reductive carbonylation of other metal (e.g., Ir and Os) salts on a silica surface added with a strong base such as NaOH.[13]

Remarkably, when a solution of $Na_2[PtCl_6]$ and CH_3CO_2Na (molar ratio Pt:Na = 1:10−1:30) in water, without added silica, is stirred overnight, evaporated to dryness, and then exposed to CO at atmospheric pressure and room temperature in the closed reaction vessel as described above, *no* carbonyl compound is formed as evidenced by infrared spectroscopy. An increase of the temperature to 100 °C leads to the formation of metallic platinum. This observation shows clearly that *silica plays a key role* during the reductive carbonylation of platinum salts into carbonyl clusters.

Working in methanol solution, $[Pt_{12}(CO)_{24}]^{2-}$ was obtained starting from $Na_2[PtCl_6]$ and NaOH (molar ratio Pt:Na = 1:6), stirring the resulting solution under a *vigorous flow* of CO for 24 h (80% yield).[15] An advantage of our silica-mediated synthesis is that it requires a much lower CO amount (only the vessel volume) to reach similar yields.

Pure $[Pt_{12}(CO)_{24}]^{2-}$ has never been obtained on the highly basic MgO surface. It was obtained along with $[Pt_9(CO)_{12}]^{2-}$ by treatment of $[Pt(\eta^3\text{-}C_3H_5)_2]$ supported on MgO with a stream of equimolar CO + H_2.[21] Yields were not reported, while the synthesis of the starting material diallylplatinum precursor is not simple.[22] $[Pt_{12}(CO)_{24}]^{2-}$ has also been generated inside the cages of zeolites, where it is entrapped (ship-in-a-bottle) and cannot be recovered. For instance, when $[Pt(NH_3)_4]^{2+}$-exchanged NaY zeolite (Si/Al molar ratio = 5.6) is calcinated (O_2, 300 °C, 2 h) and then heated under CO at 100 °C, $[Pt_{12}(CO)_{24}]^{2-}$ is formed, whereas, without calcination, the cluster $[Pt_9(CO)_{12}]^{2-}$ is generated. Unexpectedly, under similar conditions but using a more basic zeolite NaX (Si/Al molar ratio = 2.3), the cluster of higher nuclearity $[Pt_{15}(CO)_{30}]^{2-}$ was reported to be formed.[23]

When working on the silica surface, it is known that the metal loading may be an important parameter that influences the selectivity of the reductive carbonylation of various metal salts.[13] In the present work we found that the selectivity of the reductive carbonylation of $Na_2[PtCl_6]$ supported on silica in the presence of CH_3COONa can also be tuned by changing the metal loading. In fact with a 30 wt % of platinum as $Na_2[PtCl_6]$ on silica (instead of 3%), working in the presence of CH_3CO_2Na (molar ratio Pt:Na = 1:20 or 1:40) and under similar temperature and

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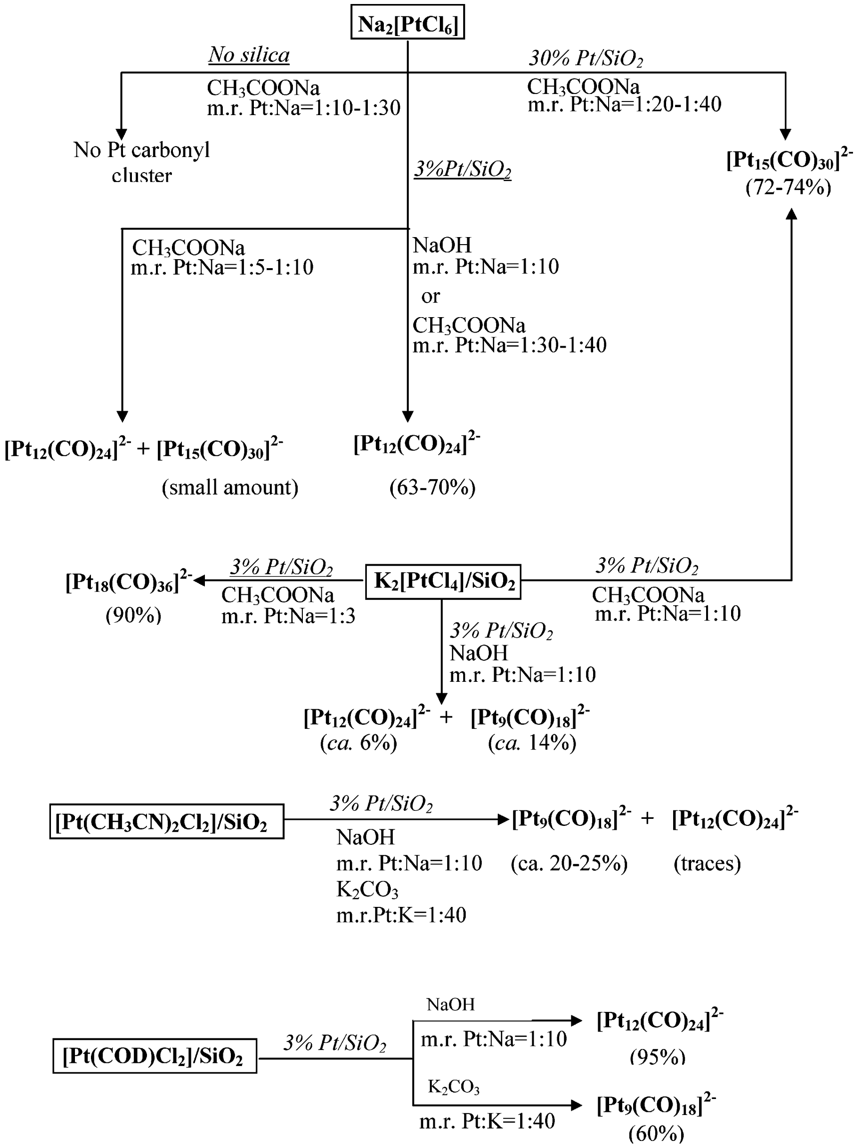
Scheme 1. Reductive Carbonylation (1 atm CO) at Room Temperature of Various Platinum Salts



CO pressure, the cluster $[PPN]_2[Pt_{15}(CO)_{30}]$ is obtained (72−73% yield, see Table 1 and Scheme 1) instead of $[PPN]_2[Pt_{12}(CO)_{24}]$.

The synthesis of the cluster $[Pt_{15}(CO)_{30}]^{2-}$ was reported to occur on the MgO surface in 73% yield by reductive carbonylation of $Na_2[PtCl_6]$, but working in the presence of traces of a solvent (MeOH), which is necessary to allow the reaction. The authors explained that the solvent protects the platinum complex by providing resistance to mass transfer of oxygen.[18]

Working in methanol solution, $[Pt_{15}(CO)_{30}]^{2-}$ was obtained starting from $Na_2[PtCl_6]$ added with various base amounts such as NaOH (molar ratio Pt:Na = 1:5.5) or CH_3COONa (molar ratio Pt:Na = 1:10) and stirring the resulting solution under a *vigorous flow* of CO for 24 h (yield 65−80%).[15]

The formation of $[Pt_{15}(CO)_{30}]^{2-}$ instead of $[Pt_{12}(CO)_{24}]^{2-}$ by increasing the metal loading from 3 to 30 wt % Pt with respect to silica can be attributed to a lower local surface basicity, although working with the same ratio Pt:CH_3CO_2Na, due to the partial neutralization of the local basicity by the HCl evolved in the reductive carbonylation. This is a known effect,[24] which can also explain the unexpected formation of $[Pt_{15}(CO)_{30}]^{2-}$ by reductive carbonylation of $[PtCl_6]^{2-}$ on the highly basic MgO surface since a lower local surface basicity is caused by the formation of MgCl acidic sites during the reduction, as proposed for the reductive carbonylation of $RhCl_3{\cdot}nH_2O$ supported on MgO, which unexpectedly affords the neutral cluster $[Rh_6(CO)_{16}]$.[24]

Reductive Carbonylation of Silica-Supported $K_2[PtCl_4]$ in the Presence of Various Bases. In order to study the influence of the oxidation state and the number of chloride ligands of the coordination sphere on the selectivity, we investigated the use as starting material of a Pt(II) salt, such as $K_2[PtCl_4]$.[25]

When a slurry of silica, $K_2[PtCl_4]$ (3 wt % Pt with respect to silica), and CH_3CO_2Na (molar ratio Pt:Na = 1:3) dissolved in the proper amount of water is stirred overnight at room temperature, evaporated to dryness, and exposed to CO at atmospheric pressure and room temperature for 48 h in the closed reaction cylindrical Pyrex vessel as above,[3] the anionic cluster $[Pt_{18}(CO)_{36}]^{2-}$ is obtained. Extraction of the silica powder with degassed methanol, followed by addition of [PPN]Cl to the methanolic solution, leads to the precipitation of the cluster

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$[PPN]_2[Pt_{18}(CO)_{36}]$ (90% yield, see Table 1 and Scheme 1), as confirmed by IR spectroscopy (THF solution, $\nu_{CO} = 2065$(vs), 1875(s) cm^{-1}). To our knowledge $[Pt_{18}(CO)_{36}]^{2-}$ has never been synthesized on MgO, probably due to the high basicity of the surface, which does not allow the formation of this Pt cluster even if some local acidic MgCl sites are generated during the reaction.

Working in methanol solution, pure $[Pt_{18}(CO)_{36}]^{2-}$ was obtained only starting from $[Pt_{12}(CO)_{24}]^{2-}$ and adding $Na_2[PtCl_6]$ drop by drop (molar ratio $[Pt_{12}(CO)_{24}]^{2-}$:Na_2PtCl_6 = 1:1) under a flow of CO (67% yield).[15] When a major amount of base is added to the silica surface, as expected a lower nuclearity cluster is obtained. In fact, when a slurry of silica, $K_2[PtCl_4]$ (3 wt % Pt with respect to silica), and CH_3CO_2Na (molar ratio Pt:Na = 1:10 or 1:40), dissolved in the proper amount of water, is stirred overnight at room temperature, evaporated to dryness, and then exposed to CO at atmospheric pressure and room temperature for 72 h in a closed reaction cylindrical Pyrex vessel as above,[3] only $[Pt_{15}(CO)_{30}]^{2-}$ is obtained, which can be easily extracted from the silica powder with degassed methanol. By addition of [PPN]Cl to the solution, precipitation of the cluster $[PPN]_2[Pt_{15}(CO)_{30}]$ occurs (74% yield; see Table 1 and Scheme 1), as confirmed by IR spectroscopy (THF solution, $\nu_{CO} = 2055$ (vs), 1873 (s) cm^{-1}).

A further increase of the surface basicity (using NaOH instead of CH_3CO_2Na) leads to the formation of anionic carbonyl clusters of even lower nuclearity. However yields become relatively low, as usually occurs when working with a very high surface basicity generated by addition of NaOH. Thus use of NaOH (molar ratio Pt:Na = 1:10), under the same reaction conditions, affords in ca. 20% yield a mixture of $[Pt_{12}(CO)_{24}]^{2-}$ and $[Pt_9(CO)_{18}]^{2-}$ (ca. 70:30 molar ratio; see Scheme 1), as confirmed by IR spectroscopy (THF solution, $\nu_{CO} = 2043$ (vs), 1862 (s) cm^{-1} for $[Pt_{12}(CO)_{24}]^{2-}$, and 2030 (vs), 1840(s) cm^{-1} for $[Pt_9(CO)_{18}]^{2-}$).

The formation of $[Pt_9(CO)_{18}]^{2-}$ was reported on the MgO surface. When $[Pt(^3\eta\text{-}C_3H_5)_2]$ is supported on MgO and the resulting powder exposed to a stream of CO, some $[Pt_9(CO)_{18}]^{2-}$ is obtained,[21] but no yield has been reported. Moreover, as mentioned above, the synthesis of η^3-diallylplatinum is not simple.[22] The cluster $[Pt_9(CO)_{18}]^{2-}$ can also be prepared with yields of ca. 50% starting from $[Pt(acac)_2]$ supported on MgO but under high pressure (CO, 100 atm).[26]

Working in solution, pure $[Pt_9(CO)_{18}]^{2-}$ was obtained by stirring Na_2PtCl_6 and NaOH (molar ratio Pt:Na = 1:9) dissolved in methanol under a *vigorous flow of CO* for 24 h (65–80% yields).[15]

Reductive Carbonylation of Silica-Supported $[Pt(CH_3CN)_2Cl_2]$ or $[Pt(COD)Cl_2]$ in the Presence of Various Bases. As described above, reductive carbonylation on the silica surface of $K_2[PtCl_4]$ in the presence of a large amount of NaOH can lead to the nonselective synthesis in low yield of the low-nuclearity cluster $[Pt_9(CO)_{18}]^{2-}$. Such low yield and selectivity could be due to a local increase of acidity due to the release of HCl during the reduction. Therefore we investigated the reductive carbonylation starting with $[Pt(CH_3CN)_2Cl_2]$, a Pt(II) compound with a lower amount of chloride ligands. When a slurry of silica, $[Pt(CH_3CN)_2Cl_2]$ (3 wt % Pt with respect to silica) dissolved in CH_3CN, and NaOH (molar ratio Pt:Na = 1:10) dissolved in MeOH is stirred overnight at room temperature, evaporated to dryness under vacuum, and then exposed to CO at atmospheric pressure and room temperature for 72 h in a closed reaction cylindrical Pyrex vessel as above,[3] $[Pt_9(CO)_{18}]^{2-}$ is obtained, along with traces of $[Pt_{12}(CO)_{24}]^{2-}$ although still in low yield. Extraction of the silica powder with degassed methanol, followed by addition of $[Bu_4N]Cl$ to the solution, leads to the precipitation of $[Bu_4N]_2[Pt_9(CO)_{18}]$, contaminated by traces of $[Pt_{12}(CO)_{24}]^{2-}$ (ca. 20–25% yield, see Table 1 and Scheme 1), as confirmed by IR spectroscopy (THF solution, $\nu_{CO} = 2030$ (vs), 1840 (s) cm^{-1}). A similar result is obtained by using a large amount of K_2CO_3 (molar ratio Pt:K = 1:40) instead of NaOH. Such low yields would suggest a negative effect of the rather polar CH_3CN basic ligand probably interacting with the silica surface and thus introducing another effect that produces a shield to the surface basicity.

In order to increase the yield of $[Pt_9(CO)_{18}]^{2-}$, we investigated the use of a less polar ligand such as *cis,cis*-1,5-cyclooctadiene (COD). Thus we studied the reductive carbonylation of $[Pt(COD)Cl_2]$. When a slurry of silica, $[Pt(COD)Cl_2]$ (3 wt % Pt with respect to silica) dissolved in CH_3CN, and K_2CO_3 (molar ratio Pt:K = 1:40) dissolved in MeOH is stirred overnight at room temperature, evaporated to dryness under vacuum, and then exposed to CO at atmospheric pressure and room temperature for 72 h in a closed reaction cylindrical Pyrex vessel as above,[3] only $[Pt_9(CO)_{18}]^{2-}$ is obtained. Extraction of the silica powder with degassed methanol, followed by addition of $[Bu_4N]Cl$ to the solution, leads to the precipitation in good yields of $[Bu_4N]_2[Pt_9(CO)_{18}]$ (60% yield; see Table 1 and Scheme 1), as confirmed by IR spectroscopy (THF solution, $\nu_{CO} = 2030$ (vs), 1840 (s) cm^{-1}). Remarkably, the use of a strong base such as NaOH (molar ratio Pt:Na = 1:10) instead of K_2CO_3 affords, working under the same conditions, only $[Pt_{12}(CO)_{24}]^{2-}$ in very high yield (95%). This latter is an unexpected result since usually the high basicity of the silica surface obtained by addition of NaOH produces with lower yield a cluster of lower nuclearity (see above).

Conclusion

This work is another example of the flexibility of the use of the silica surface in the presence of bases for high-yield and selective syntheses of a series of metal carbonyl clusters starting from easily available materials. We have reported in fact the selective syntheses in a very simple way of the various platinum carbonyl dianion $[Pt_3(CO)_6]_n^{2-}$ (n = 6, 5, 4, 3) clusters, first synthesized in solution by Longoni and Chini.[15] Yields and selectivities are usually comparable or even higher than those in solution, but reaction conditions are simpler and require a much lower CO amount (only the vessel volume). In particular, the one-step silica-mediated synthesis of $[Pt_{18}(CO)_{36}]^{2-}$ from $K_2[PtCl_4]$ (90% yield) is very convenient when compared to the traditional synthesis in methanol solution, which requires two steps: (i) formation of $[Pt_{12}(CO)_{24}]^{2-}$ and (ii) addition of $Na_2[PtCl_6]$ drop by drop (molar ratio $[Pt_{12}(CO)_{24}]^{2-}$:$Na_2[PtCl_6]$ = 1:1) under a flow of CO (67% yield). Similarly, the silica-mediated synthesis of $[Pt_{12}(CO)_{24}]^{2-}$ from $[Pt(COD)Cl_2]$ (95% yield) is appealing with respect to the synthesis in solution (80% yield), which involves reduction under a *vigorous* flow of CO of $Na_2[PtCl_6]$ in the presence of NaOH (molar ratio Pt:Na = 1:6). In this work we have clearly shown that the selectivity and yields of the silica-mediated reductive carbonylation reaction are tuned by controlling not only the surface loading and the basicity of the surface but also the amount of HCl evolved in the reductive carbonylation, which may strongly influence the local basicity or the polarity of neutral ligands of the coordination sphere of platinum. We have also confirmed that the role of the silica surface is not only that of a reaction medium but

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is fundamental in these reductive carbonylations since *no* carbonyl cluster is formed, in the absence of silica, by treatment of a Pt salt, such as $Na_2[PtCl_6]$, under similar reaction conditions. Thus, the deposition of Pt salts on the silica surface or even their simple interaction with a silica support produces a high and selective reactivity toward reductive carbonylation.

In conclusion once again we have shown that the silica surface can be an unusual and useful reaction medium to produce carbonyl clusters with yields and selectivity not only easily tunable but also in some cases higher than those obtained by using traditional techniques in solution.[13]

Experimental Section

General Comments. SiO_2 (Aerosil 200 Degussa, with a nominal surface area of 200 m^2/g) was used after treatment in vacuum (10^{-2} Torr) at 25 °C for 3 h. $Na_2[PtCl_6]$ was purchased from Strem Chemicals, $[Pt(CH_3CN)_2Cl_2]$ and $[Pt(COD)Cl_2]$ were purchased from Sigma Aldrich, while $K_2[PtCl_4]$ was prepared according to the literature.[25] All reaction products were identified, after extraction from silica, by infrared spectroscopy, their spectra being compared to those of pure samples.[15] Elemental analyses were carried out in the Dipartimento di Chimica Inorganica, Metallorganica e Analitica of the Milan University.

Preparation of Silica-Supported $Na_2[PtCl_6]$ (3 wt % Pt/SiO_2) Added with Bases. A slurry of silica (4.63 g), $Na_2[PtCl_6]\cdot 6H_2O$ (0.4 g, 0.712 mmol, 3 wt % Pt/SiO_2), degassed H_2O (ca. 150 mL), and CH_3CO_2Na or NaOH (correct amount to have the desired molar ratio Na:Pt) was stirred overnight in a 250 mL two-necked flask under N_2 at 25 °C. The solvent was evaporated under vacuum (10^{-2} Torr) using a water bath at 80 °C. The final yellow powder was stored under N_2.

Preparation of Silica-Supported $Na_2[PtCl_6]$ (30 wt % Pt/SiO_2) Added with Bases. A slurry of silica (4.50 g), $Na_2[PtCl_6]\cdot 6H_2O$ (3.9 g, 6.94 mmol, 30 wt % Pt/SiO_2), degassed H_2O (ca. 150 mL), and CH_3CO_2Na (correct amount to have the desired molar ratio Na:Pt) was stirred overnight in a 250 mL two-necked flask under N_2 at 25 °C. The solvent was evaporated under vacuum (10^{-2} Torr) using a water bath at 80 °C. The final yellow powder was stored under N_2.

Preparation of Silica-Supported $K_2[PtCl_4]$ (3 wt % Pt/SiO_2) Added with Bases. A slurry of silica (4.00 g), $K_2[PtCl_4]$ (0.255 g, 0.615 mmol, 3 wt % Pt/SiO_2), degassed H_2O (ca. 150 mL), and CH_3CO_2Na or NaOH (correct amount to have the desired molar ratio Na:Pt) was stirred overnight in a 250 mL two-necked flask under N_2 at 25 °C. The solvent was evaporated under vacuum (10^{-2} Torr) using a water bath at 80 °C. The final gray powder was stored under N_2.

Preparation of Silica-Supported $[Pt(CH_3CN)_2Cl_2]$ (3 wt % Pt/SiO_2) Added with Bases. $[Pt(CH_3CN)_2Cl_2]$ (0.25 g, 0.718 mmol, 3 wt % Pt/SiO_2) was dissolved in degassed CH_3CN (ca. 100 mL), NaOH or K_2CO_3 (correct amount to have the desired molar ratio Pt:Na or Pt:K) was dissolved in degassed MeOH (ca. 50 mL), and then the two above-mentioned solutions were joined in a 250 mL two-necked flask with silica (4.68 g). The resulting slurry was stirred overnight under N_2 at 25 °C and evaporated to dryness under vacuum (10^{-2} Torr) using a water bath at 80 °C. The final light yellow powder was stored under N_2.

Preparation of Silica-Supported $[Pt(COD)Cl_2]$ (3 wt % Pt/SiO_2) Added with Bases. $[Pt(COD)Cl_2]$ (0.250 g, 0.67 mmol, 3 wt % Pt/SiO_2) was dissolved in degassed CH_3COCH_3 (ca. 100 mL), NaOH or K_2CO_3 (correct amount to have the desired molar ratio Pt:Na or Pt:K) was dissolved in degassed MeOH (ca. 50 mL), and then the two above-mentioned solutions were joined in a 250 mL two-necked flask with silica (4.35 g). The resulting slurry was stirred overnight under N_2 at 25 °C and evaporated to dryness under vacuum (10^{-2} Torr) using a water bath at 80 °C. The final light yellow powder was stored under N_2.

Synthesis of $[PPN]_2[Pt_{18}(CO)_{36}]$. A slurry of silica (4.00 g), $K_2[PtCl_4]$ (0.255 g, 0.614 mmol; 3 wt % Pt/SiO_2), anhydrous CH_3CO_2Na (0.151 g, 1.84 mmol, molar ratio Pt:Na = 1:3), and degassed H_2O (150 mL) was stirred in a 250 mL two-necked flask under N_2 for 24 h at room temperature, affording a yellow mixture. The solvent was evaporated at rt under vacuum (10^{-2} Torr) using a water bath at 80 °C, and the resulting gray powder was transferred into a cylindrical Pyrex vessel (diameter 40 mm, length 350 mm) under a N_2 flow. The powder was treated under vacuum (10^{-2} Torr), then exposed to CO (1 atm) for 48 h at rt. Extraction of the resulting very dark green powder under N_2 onto a porous septum with MeOH (ca. 150 mL) afforded a green solution (ν_{CO} in MeOH: 2066 cm^{-1} (s), 1880 cm^{-1} (m)). Concentration of the solution up to 50 mL, followed by addition of bis(triphenylphosphoranylidene)ammonium chloride (PPNCl ca. 0.3 g), led to precipitation of pure green $[PPN]_2[Pt_{18}(CO)_{36}]$ (ν_{CO} in THF: 2065 (vs), 1875 (s) cm^{-1}) with a 90% yield (0.172 g). Anal. Found (calcd): C 23.19 (23.16), H 1.08 (1.07), N 0.50 (0.50).

Synthesis of $[PPN]_2[Pt_{15}(CO)_{30}]$. (a) From $Na_2[PtCl_6]$. A slurry of silica (4.50 g), $Na_2[PtCl_6]\cdot 6H_2O$ (3.9 g, 6.94 mmol, 30 wt % Pt with respect to SiO_2), anhydrous CH_3CO_2Na (11.3 g, 0.138 mol, molar ratio Pt:Na = 1:20), and degassed H_2O (150 mL) was stirred in a 250 mL two-necked flask under N_2 for 24 h at room temperature, affording a yellow mixture. The solvent was evaporated at rt under vacuum (10^{-2} Torr) using a water bath at 80 °C, and the resulting yellow powder was transferred into a cylindrical Pyrex vessel (diameter 40 mm, length 350 mm) under a N_2 flow. The powder was treated under vacuum (10^{-2} Torr), then exposed to CO (1 atm) for 48 h at rt. Extraction of the resulting dark green powder under N_2 onto a porous septum with MeOH (ca. 150 mL) afforded a brilliant green solution (ν_{CO} 2062 cm^{-1} (s), 1881 cm^{-1} (m)). Concentration of the solution to 50 mL, followed by addition of PPNCl (ca. 0.3 g), led to the precipitation of pure green $[PPN]_2[Pt_{15}(CO)_{30}]$ (2055 cm^{-1} (s), 1874 cm^{-1} (m)) with a 72% yield (1.613 g). Anal. Found (calcd): C 25.36 (25.27), H 1.25 (1.24), N 0.59 (0.58).

(b) From $K_2[PtCl_4]$. A slurry of silica (4.00 g), $K_2[PtCl_4]$ (0.255 g, 0.615 mmol; 3 wt % Pt with respect to SiO_2), anhydrous CH_3CO_2Na (0.504 g, 6.15 mmol, molar ratio Pt:Na = 1:10), and degassed H_2O (150 mL) was stirred in a 250 mL two-necked flask under N_2 for 24 h at room temperature, affording a yellow mixture. The solvent was evaporated at rt under vacuum (10^{-2} Torr) using a water bath at 80 °C, and the resulting gray powder was transferred into a cylindrical Pyrex vessel (diameter 40 mm, length 350 mm) under a N_2 flow. The powder was treated under vacuum (10^{-2} Torr), then exposed to CO (1 atm) for 48 h at rt. Extraction of the resulting very dark green powder under N_2 onto a porous septum with MeOH (ca. 150 mL) afforded a green solution (ν_{CO} 2062 cm^{-1} (s), 1881 cm^{-1} (m)). Concentration of the solution up to 50 mL, followed by addition of [PPN]Cl (ca. 0.3 g), afforded pure green $[PPN]_2[Pt_{15}(CO)_{30}]$, which precipitated (2055 cm^{-1} (s), 1874 cm^{-1} (m)) with a 74% yield (0.147 g). Anal. Found (calcd): C 25.32 (25.27), H 1.25 (1.24), N 0.58 (0.58).

Synthesis of $[PPN]_2[Pt_{12}(CO)_{24}]$. (a) From $Na_2[PtCl_6]$. A slurry of silica (4.63 g), $Na_2[PtCl_6].6H_2O$ (0.4 g, 0.712 mmol; 3 wt % Pt with respect to SiO_2), anhydrous CH_3CO_2Na (2.33 g, 28.4 mmol, molar ratio Pt:Na = 1:40), and degassed H_2O (150 mL) was stirred in a 250 mL two-necked flask under N_2 for 24 h at room temperature, affording a yellow mixture. The solvent was evaporated at rt under vacuum (10^{-2} Torr) using a water bath at 80 °C, and the resulting yellow powder was transferred into a cylindrical Pyrex vessel (diameter 40 mm, length 350 mm) under a N_2 flow. The powder was treated under vacuum (10^{-2} Torr), then exposed to CO (1 atm) for 48 h at rt. Extraction of the resulting dark green powder under N_2 onto a porous septum with MeOH (ca. 150 mL) afforded a green solution (ν_{CO} 2058 cm^{-1} (s), 1873 cm^{-1} (m)). Concentration of the solution up to 50 mL, followed by addition of [PPN]Cl (ca. 0.3 g), afforded pure green $[PPN]_2[Pt_{12}(CO)_{24}]$, which precipitated ($\nu_{CO}$ in THF: 2043 cm^{-1} (s), 1862 cm^{-1} (m)) with a 70% yield (0.170 g). Anal. Found (calcd): C 28.23 (28.16), H 1.48 (1.47), N 0.69 (0.68).

(b) From $[Pt(COD)Cl_2]$. A solution of $[Pt(COD)Cl_2]$ (0.25 g, 0.67 mmol, 3 wt % Pt/SiO$_2$) in degassed CH_3COCH_3 (ca. 100 mL) and a solution of NaOH (0.268 g., 6.7 mmol, molar ratio Pt:Na = 1:10) in degassed MeOH (ca. 50 mL) were joined in a 250 mL two-necked flask with silica (4.35 g). The reaction mixture was stirred overnight under N_2 at 25 °C and then evaporated to dryness under vacuum (10^{-2} Torr) using a water bath at 80 °C. The resulting yellow powder was transferred into a cylindrical Pyrex vessel (diameter 40 mm, length 350 mm) under a N_2 flow. The powder was treated under vacuum (10^{-2} Torr), then exposed to CO (1 atm) for 72 h at rt. Extraction of the resulting dark green powder under N_2 onto a porous septum with MeOH (ca. 150 mL) afforded a green solution (ν_{CO} 2058 cm^{-1} (s), 1873 cm^{-1} (m)). Concentration of the solution up to 50 mL, followed by addition of [PPN]Cl (ca. 0.3 g), afforded pure green $[PPN]_2[Pt_{12}(CO)_{24}]$, which precipitated ($\nu_{CO}$ in THF: 2043 cm^{-1} (s), 1862 cm^{-1} (m)) with a 95% yield (0.217 g). Anal. Found (calcd): C 28.10 (28.16), H 1.46 (1.47), N 0.68 (0.68).

Synthesis of $[Bu_4N]_2[Pt_9(CO)_{18}]$. (a) From $[Pt(CH_3CN))Cl_2]$. A solution of $[Pt(CH_3CN)_2Cl_2]$ (0.25 g, 0.718 mmol, 3 wt % Pt/SiO$_2$) in degassed CH_3CN (ca. 100 mL) and a solution of NaOH (0.29 g, 7.25 mmol, molar ratio Pt:Na = 1:10) in degassed MeOH (ca. 50 mL) were joined in a 250 mL two-necked flask with silica (4.68 g). The reaction mixture was stirred overnight under N_2 at 25 °C and then evaporated to dryness under vacuum (10^{-2} Torr) using a water bath at 80 °C. The resulting yellow powder was transferred into a cylindrical Pyrex vessel (diameter 40 mm, length 350 mm) under a N_2 flow. The powder was treated under vacuum (10^{-2} Torr), then exposed to CO (1 atm) for 72 h at rt. Extraction of the resulting dark red powder under N_2 onto a porous septum with MeOH (ca. 150 mL) afforded a red solution. Concentration of the solution to 50 mL, followed by addition of $[Bu_4N]Cl$ (ca. 0.3 g) dissolved in 10 mL of water, afforded dark red $[Bu_4N]_2[Pt_9(CO)_{18}]$, which precipitated (ν_{CO} in THF: 2030 cm^{-1} (vs), 1840 cm^{-1} (s)) contaminated by traces of $[Bu_4N]_2[Pt_{12}(CO)_{24}]$ with ca. 25% yield (0.0548 g).

(b) From $[Pt(COD)Cl_2]$. A solution of $[Pt(COD)Cl_2]$ (0.25 g, 0.67 mmol, 3 wt % Pt/SiO$_2$) in degassed CH_3COCH_3 (ca. 100 mL) and a solution of K_2CO_3 (1.85 g, 26.8 mmol, molar ratio Pt:K = 1:40) in degassed MeOH (ca. 50 mL) were joined in a 250 mL two-necked flask with silica (4.35 g). The reaction mixture was stirred overnight under N_2 at 25 °C and then evaporated to dryness under vacuum (10^{-2} Torr) using a water bath at 80 °C. The resulting yellow powder was transferred into a cylindrical Pyrex vessel (diameter 40 mm, length 350 mm) under a N_2 flow. The powder was treated under vacuum (10^{-2} Torr), then exposed to CO (1 atm) for 72 h at rt. Extraction of the resulting dark red powder under N_2 onto a porous septum with MeOH (ca. 150 mL) afforded a red solution. Concentration of the solution to 50 mL, followed by addition of $[Bu_4N]Cl$ (ca. 0.3 g) dissolved in 10 mL of water, afforded pure dark red $[Bu_4N]_2[Pt_9(CO)_{18}]$, which precipitated (ν_{CO} in THF: 2030 cm^{-1} (vs), 1840 cm^{-1} (s)) with 60% yield (0.123 g). Anal. Found (calcd): C 21.93 (21.87), H 2.63 (2.62), N 1.03 (1.02).

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