Formation of [Ir(CO)₂Cl]ₓ (x = 2, n) Species by Mild Carbonylation of [Ir(cyclooctene)₂Cl]₂ Supported on Silica or in Solution: A New Convenient Material for the Synthesis of Iridium(I) Carbonyl Complexes

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A pale-blue Ir(I) dicarbonyl chloride surface species is obtained by carbonylation of [Ir-(cyclooctene)₂Cl]₂ supported on the silica surface, working under mild conditions (1 atm of CO, room temperature). This species is probably weakly bound to the surface silanol groups. It can be extracted only with weak donor solvents like acetone and acetonitrile, affording a solution of the dimer [Ir(CO)₂Cl]₂. This dimer can be also obtained by carbonylation under mild conditions of [Ir(cyclooctene)₂Cl]₂ in the latter solvents. Evaporation of the donor solvents transforms [Ir(CO)₂Cl]₂ into a dark-brown, almost black, amorphous carbonyl material, probably polymeric via strong Ir—Ir interactions. Likewise, in nondonor solvents like toluene and pentane, carbonylation of [Ir(cyclooctene)₂Cl]₂ produces the same insoluble material of formula [Ir(CO)₂Cl]ₙ. This material may be reversibly dissolved by donor solvating solvents, to form again a solution of the dimer. The acetonitrile solution of [Ir-(CO)₂Cl]₂ is a very convenient starting material for the high-yield preparation of many Ir(I) carbonyl derivatives such as, for instance, [Ir(CO)₂Cl₂]⁻, [Ir(CO)₂(amine)Cl], [Ir(CO)(PPh₃)₂-Cl], and [Ir(CO)₂(acac)], where acacH is acetylacetone.

Introduction

Although [Rh(CO)₂Cl]₂ is well-known, its iridium analogue is not. It has been briefly reported that when CO is bubbled through a solution of [Ir(COT)₂Cl]₂ (COT = cyclooctene) in toluene, a deep navy-blue precipitate is formed.[1] To our knowledge, this iridium compound has never been identified nor well characterized. It was simply reported that the deep blue solid is soluble in ketones, affording a solution with carbonyl absorptions at 2075 (s) and 1990 (s) cm⁻¹.[1]

Our recent studies on the reductive carbonylation of silica-supported RhCl₃·3H₂O have shown that this rhodium salt may be easily converted into a mixture of physisorbed [Rh(CO)₂Cl]₂ and [Rh(CO)₂(H₂O)Cl] by working under 1 atm of CO at room temperature.[2,3] Differently, no reaction occurs when silica-supported IrCl₃·3H₂O is treated under similar conditions.[2] A surface "Irᴵᴵᴵ(CO)₂" species is formed at 50 °C only, while a further increase of the temperature up to 100–150 °C leads to the known species [Ir(CO)₃Cl]ₙ which sublimes.[2] Starting from IrCl₃·3H₂O, the formation of [Ir(CO)₂Cl]₂ was never detected on the silica surface. Similarly, [Ir(CO)₂Cl]₂ has not been identified during the reductive carbonylation of IrCl₃·3H₂O in solution, although it has been reported that the latter salt is converted into [Ir(CO)₂Cl₂]⁻ by refluxing in ethanol in the presence of CO.[4]

During our recent investigations of the surface orga-

nometallic chemistry of different salts or complexes,[2,3,5] we discovered that carbonylation reactions can occur with a high selectivity under mild conditions when working on silica. Therefore it was worth attempting the surface synthesis of the enigmatic [Ir(CO)₂Cl]₂ complex starting from a Ir(I) complex such as [Ir-(COT)₂Cl]₂ (COT = cyclooctene) physisorbed on silica. Besides, it is well-known that the surface of silica may be considered as a solid donor ligand, due to its surface silanol groups.[3,6] For the sake of comparison, the carbonylation of [Ir(COT)₂Cl]₂ in donor and nondonor solvents was also investigated.

Results and Discussion

Carbonylation of [Ir(COT)₂Cl]₂ Supported on SiO₂. When [Ir(COT)₂Cl]₂ supported on a wafer of silica is exposed to CO at atmospheric pressure, the color of the solid changes immediately from yellow to blue. After 1 h it is still pale-blue, and its infrared spectrum shows the presence of two strong carbonyl bands at 2086 (s) and 2007 (s) cm⁻¹. These bands suggest a "Irᴵ(CO)₂" surface species since their positions are quite similar to those reported by Tanaka *et al.*[7] for "Irᴵ(CO)₂"

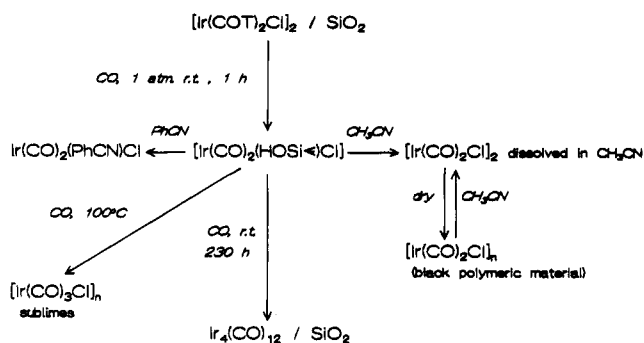† Dipartimento di Chimica Inorganica, Metallorganica, e Analitica.
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Scheme 1

[Ir(COT)₂Cl]₂ / SiO₂

CO, 1 atm, r.t., 1 h

PhCN   CH₃CN

Ir(CO)₂(PhCN)Cl ◄— [Ir(CO)₂(HOSi≡)Cl] —► [Ir(CO)₂Cl]₂ dissolved in CH₃CN

CO, 100°C   CO, r.t. 230 h   dry ‖ CH₃CN

[Ir(CO)₃Cl]ₙ sublimes   [Ir(CO)₂Cl]ₙ (black polymeric material)

Ir₄(CO)₁₂ / SiO₂

fragments covalently bound to the silica surface (2080 (s) and 2008 (s) cm⁻¹. The position, shape, and intensity of the carbonyl absorptions are also quite similar to those reported for [Rh(CO)₂(H₂O)Cl] physisorbed on silica (2084 (s) and 2012 (s) cm⁻¹) but different from those of [Rh(CO)₂Cl]₂ physisorbed on silica, which is characterized by three bands at 2104 (w), 2089 (s), and 2033 (s) cm⁻¹.[2] Similar to the easy conversion of physisorbed [Rh(CO)₂(H₂O)Cl] to [Rh₆(CO)₁₆],[2] further treatment of the "Irᴵ(CO)₂" surface species under CO at room temperature for 19 h leads to the appearance of two new bands at 2072 (s) and 2034 (m) cm⁻¹, typical of [Ir₄(CO)₁₂] molecularly dispersed on the silica surface.[8] By prolonged treatment under CO, the two bands at 2086 and 2007 cm⁻¹ decrease in intensity with parallel growth of the other two bands. After a total of 230 h under the same conditions, the conversion into [Ir₄(CO)₁₂] molecularly dispersed on the silica surface is almost complete, as judged from the infrared spectrum (Scheme 1). When [Ir(COT)₂Cl]₂ supported on silica is heated at 100 °C under CO, [Ir(CO)₃Cl]ₙ[9] sublimes on the cold part of the reaction vessel. These data suggest that the pale-blue intermediate surface iridium dicarbonyl compound is a "Ir(CO)₂Cl" surface species. In order to study how it is bound to the silica surface, we tried to recover the surface complex by extraction with different solvents.

When a powder sample of [Ir(COT)₂Cl]₂ supported on silica is treated with CO for 20 h, the "Irᴵ(CO)₂" species is obtained along with some [Ir₄(CO)₁₂]. Attempts to extract the iridium(I) carbonyl species from the silica surface with nondonor solvents such as toluene and chloroform failed, while physisorbed [Rh(CO)₂Cl]₂ and [Rh(CO)₂(H₂O)Cl] are easily extracted by these solvents.[2] This suggests some chemical interaction between iridium and surface silanol groups.[3] Extraction at room temperature with acetonitrile affords a yellow solution with an infrared spectrum similar to that of the pale-blue silica-supported iridium dicarbonyl species (ν(CO) = 2085 (s) and 2008 (s) cm⁻¹) along with very minor amounts of [Ir(CO)₂Cl₂]⁻ (ν(CO) = 2055 (w) and 1972 (w) cm⁻¹).[10] The mass spectrum of the resultant acetonitrile solution shows clearly the presence of the dimer [Ir(CO)₂Cl]₂. Therefore, the "Irᴵ(CO)₂" species formed on the silica surface is not bound to the surface by a strong covalent Ir—OSi bond. It could be a species weakly interacting with the surface silanol groups such as [Ir(CO)₂(HOSi≡)Cl].

Although the infrared spectra of the surface species and of the species in acetonitrile solution are very similar, the different color and the lack of extraction with a nondonor solvating solvent do suggest that they are different. By analogy with other related metal acetonitrile complexes,[11] such as the known [Rh(CO)₂(CH₃CN)Cl],[12] it is expected that a species such as [Ir(CO)₂(CH₃CN)Cl] would show a ν(CN) higher than that of free acetonitrile. Now, when the silica-supported "Ir(CO)₂Cl" species is extracted with a mixture of acetonitrile and chloroform to form a yellow solution, only free acetonitrile is shown by infrared spectroscopy, suggesting that the iridium(I) dicarbonyl species in acetonitrile is not [Ir(CO)₂(CH₃CN)Cl]. The infrared and mass spectra would suggest that most probably it is [Ir(CO)₂Cl]₂ strongly solvated.

In order to confirm this statement, we reinvestigated the reactivity of the well-known [Rh(CO)₂Cl]₂ complex with acetonitrile.[12] Addition of acetonitrile to a yellow solution of [Rh(CO)₂Cl]₂ in chloroform lightens the color's solution and causes a change of the carbonyl absorptions from 2109 (w), 2094 (s), and 2036 (s) cm⁻¹ to 2097 (s) and 2029 (s) cm⁻¹, but only free acetonitrile is present, as shown by infrared spectroscopy. It is known that [Rh(CO)₂(CH₃CN)Cl] can be formed only at very low temperatures.[12] Besides, it has been reported that the weak carbonyl band at 2109 cm⁻¹, characteristic of the [Rh(CO)₂Cl]₂ species, is due to a bent "booklike structure" with chloride bridges.[13] Since addition of acetonitrile causes the disappearance of this weak CO absorption, probably, in this solvent, the rhodium dimer is distorted into a dimeric planar chlorine bridge structure due to a strong solvation which would account also for the observed shift of the infrared frequencies. In conclusion, the similar behavior in acetonitrile solution would confirm that the iridium(I) dicarbonyl species described above is [Ir(CO)₂Cl]₂ strongly solvated by acetonitrile.

Extraction of the silica-supported "Ir(CO)₂Cl" species with a mixture of benzonitrile and chloroform affords [Ir(CO)₂(PhCN)Cl], as suggested by the infrared spectrum of the resulting solution which shows a ν(CN) at 2279 cm⁻¹, 47 cm⁻¹ higher than that in free benzonitrile, while the carbonyl absorptions appear at 2085 (s) and 2012 (s) cm⁻¹. The higher stability of [Ir(CO)₂(PhCN)Cl] compared to [Ir(CO)₂(CH₃CN)Cl] is not surprising since complexes of the type [Rh(CO)₂(nitrile)Cl] are stable even at room temperature in the case of aromatic nitriles.[12] In fact, we observed that addition of benzonitrile to [Rh(CO)₂Cl]₂ in chloroform affords [Rh(CO)₂(PhCN)Cl] characterized by two strong carbonyl bands at 2098 (s) and 2029 (s) cm⁻¹ and a coordinated nitrile band at 2278 (w) cm⁻¹. Therefore, the behavior toward nitriles of the iridium(I) dicarbonyl species parallels that of [Rh(CO)₂Cl]₂. In conclusion, the iridium dicarbonyl species formed on the silica surface is probably a [Ir(CO)₂(HOSi≡)Cl] species, this alternative being possible since surface silanols are very weak ligands which can

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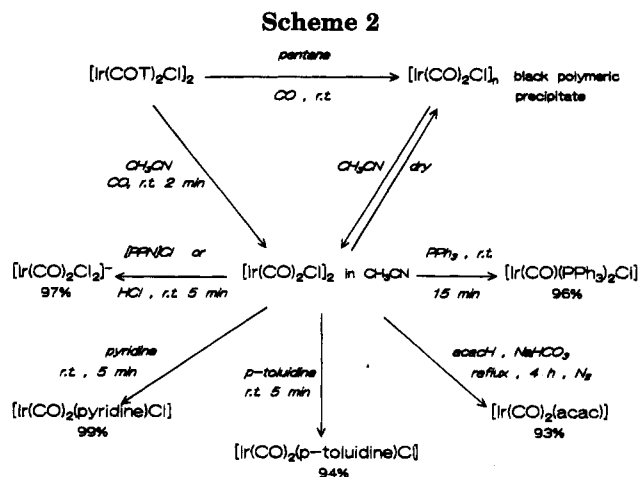
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Scheme 2

[Ir(COT)₂Cl]₂ —— *pentane* / CO, r.t. ——→ [Ir(CO)₂Cl]ₙ black polymeric precipitate

CH₃CN / CO, r.t. 2 min

CH₃CN / dry

[Ir(CO)₂Cl₂]⁻ 97% ←—— [PPN]Cl or HCl, r.t. 5 min —— [Ir(CO)₂Cl]₂ in CH₃CN ——→ PPh₃, r.t. 15 min ——→ [Ir(CO)(PPh₃)₂Cl] 96%

pyridine r.t., 5 min

p-toluidine r.t. 5 min

acacH, NaHCO₃ reflux, 4 h, N₂

[Ir(CO)₂(pyridine)Cl] 99%

[Ir(CO)₂(p-toluidine)Cl] 94%

[Ir(CO)₂(acac)] 93%

be displaced by the good solvation of acetonitrile, but not by nondonor solvents.[3]

The pale-blue color of the surface "Ir(CO)₂Cl" species, compared to the yellow color of [Ir(CO)₂Cl]₂ in nitriles, would suggest the existence on the silica surface of some Ir—Ir interactions. In particular, related species such as [Ir(CO)₂(amine)Cl][14] are highly colored in the solid state; other d⁸ Ir(I) carbonyl complexes are known to interact by Ir—Ir weak bonds, producing colored species such as [Ir(CO)₂(acac)] (acac = acetylacetonate anion)[15,16] or [Ir(CO)₃Cl]ₙ.[17] However, the formation of a similar high polymeric chain of stacked planar iridium carbonyl units with Ir—Ir interactions would be unlikely on the silica surface due to the rigidity of topology of the surface silanol groups and to the low Ir loading (2 wt % Ir/SiO₂). In agreement with this statement, the color and the infrared spectrum of the surface species is different from that of the black, clearly polymeric [Ir(CO)₂Cl]ₙ discussed below. Thus, the pale-blue color of the iridium dicarbonyl surface species might be due to just a few intermolecular Ir—Ir interactions, producing oligomers. Of course, an intramolecular Ir—Ir bond within a supported [Ir(CO)₂Cl]₂ species, with a bent "booklike structure", cannot be totally excluded, albeit there is not this kind of intramolecular bond within [Rh(CO)₂Cl]₂.[13] Work is in progress to determine by EXAFS the existence of this kind of Ir—Ir bond and the nature of the iridium coordination sphere.

Carbonylation of [Ir(COT)₂Cl]₂ in Solution. As soon as a yellow solution of [Ir(COT)₂Cl]₂ in toluene or pentane is exposed to CO at room temperature, an iridium carbonyl species, probably [Ir(CO)₂Cl]₂, is formed, as shown by the appearance of two weak bands at 2081 and 2006 cm⁻¹ in the infrared spectrum of the resulting yellow-green solution. Simultaneously, a dark almost black powder begins to precipitate. After 5 min, there is no [Ir(CO)₂Cl]₂ left in solution. The low solubility in nondonor solvents, the very dark color, and both thermogravimetric and elemental analysis would be in agreement with a polymeric [Ir(CO)₂Cl]ₙ species (Scheme 2; see Experimental Section). This formulation is confirmed by the mass spectrum which is in agreement

with the existence of potential [Ir(CO)₂Cl]₂ moieties in the polymeric chain. Unfortunately, the material is completely amorphous, as confirmed by X-ray powder diffraction, so that a structural analysis is not possible. Its infrared spectrum, taken as a Nujol mull, shows a very broad carbonyl band centered at about 2076 cm⁻¹, with shoulders at 2088 and 2062 cm⁻¹. The Ir—Cl absorptions appear at 327 (w, br) cm⁻¹, i.e. 48 cm⁻¹ lower than the terminal Ir—Cl stretching frequency in [Ir(CO)₃Cl]ₙ,[9] as expected for bridging Ir—Cl bonds linking the Ir(CO)₂ groups. In fact, the bridging Rh—Cl stretching frequencies in [Rh(CO)₂Cl]₂ are observed some 20–40 cm⁻¹ below those of terminal Rh—Cl stretching vibrations.[13] For comparison, we observed that the infrared absorptions of bridging Ir—Cl bonds in [Ir(COT)₂Cl]₂ are at 318 (m), 301 (w), and 272 (s) cm⁻¹.

The dark color of the [Ir(CO)₂Cl]ₙ polymer suggests a chain of strong Ir—Ir interactions. By analogy with [Ir(CO)₃Cl]ₙ,[17] this polymer is probably formed of [Ir(CO)₂Cl]₂ units linked by Ir—Cl bonds and by intermolecular Ir—Ir bonds to form [Ir(CO)₂Cl]ₙ with infinite chains. The black material dissolves in donor solvents such as acetonitrile and acetone which cleave the Ir—Ir interactions (Scheme 2). The infrared spectrum of the resultant yellow acetonitrile solution shows the typical two carbonyl absorptions at 2085 (s) and 2008 (s) cm⁻¹, as described above. In acetone the carbonyl absorptions appear at 2073 (s) and 1991 (s) cm⁻¹, similar to that reported for the enigmatic "blue iridium complex" dissolved in ketones.[1] Addition of HCl or [N(PPh₃)₂]Cl to these solutions at room temperature affords [Ir(CO)₂Cl₂]⁻ as shown by infrared spectroscopy.

Interestingly, contrarily to other Ir(I) carbonyl species characterized by a chain of weak Ir—Ir interactions such as [Ir(CO)₂(acac)][16] and [Ir(CO)₂(p-toluidine)Cl],[14] [Ir(CO)₂Cl]ₙ does not dissolve in nondonor solvents like chloroform, suggesting that its Ir—Ir interactions are particularly strong. In agreement with this suggestion, for [Ir(CO)₃Cl]ₙ which, like [Ir(CO)₂Cl]ₙ, is not soluble in nondonor solvents,[17] the Ir—Ir distance is shorter than that found in other carbonyliridium(I) species with Ir—Ir polymeric chains (e.g. [Ir(CO)₂(acac)]).[16] This observation prompted us to investigate the carbonylation of [Ir(COT)₂Cl]₂ in weak donor solvents such as acetonitrile and acetone which can act as donor solvating ligands like the silica surface.

Under nitrogen, [Ir(COT)₂Cl]₂ does not dissolve in acetonitrile. However, as soon as nitrogen is replaced by CO, the initial complex disappears and a yellow solution is obtained. Its infrared spectrum, taken 5 min after admission of CO, shows the expected bands at 2085 (s) and 2008 (s) cm⁻¹ due to the presence of the [Ir(CO)₂Cl]₂ solvated species (Scheme 2). Similarly, when a suspension of [Ir(COT)₂Cl]₂ in acetone is exposed to CO, two CO bands appear at 2073 (s) and 1991 (s) cm⁻¹. Attempts to isolate [Ir(CO)₂Cl]₂ from these solutions failed, because evaporation of the solvent leads again to black polymeric [Ir(CO)₂Cl]ₙ, as shown by infrared spectroscopy and thermogravimetric analysis (see Experimental Section).

Reactivity of the [Ir(CO)₂Cl]₂ Acetonitrile Solution. Because the iridium analogue of [Rh(CO)₂Cl]₂ was unknown, [Ir(CO)₃Cl]ₙ has been often chosen as the starting material to prepare a large range of Ir(I)

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carbonyl complexes. For example, [Ir(CO)$_2$Cl$_2$]$^-$ is obtained by reaction of [Ph$_4$As]Cl with [Ir(CO)$_3$Cl]$_n$ in ethanol under reflux for 1 h,[18] while the complexes [Ir-(CO)(PPh$_3$)$_2$Cl] and [Ir(CO)$_2$(p-toluidine)Cl] may be prepared by refluxing this iridium polymer with PPh$_3$ and p-toluidine for 24 and 12 h, respectively.[19] Thus [Ir(CO)$_3$Cl]$_n$ is less reactive than [Rh(CO)$_2$Cl]$_2$ which is converted in the same kind of products already at room temperature.[20] This observation prompted us to investigate the use of an acetonitrile solution of [Ir(CO)$_2$Cl]$_2$ as the starting material for the preparation of various iridium carbonyl complexes. It was found that [Ir-(CO)$_2$Cl]$_2$ reacts easily at room temperature with the chloride ion, pyridine, toluidine, triphenylphosphine, and acetylacetonate anion (Scheme 2).

Addition of [N(PPh$_3$)$_2$]Cl or HCl to the solution in acetonitrile causes the disappearance of the bands at 2085 (s) and 2008 (s) cm^{-1} with parallel formation of bands at 2055 (s) and 1972 (s) cm^{-1}, showing that the chloride ion is able to cleave the chloro bridge of [Ir(CO)$_2$Cl]$_2$, affording [Ir(CO)$_2$Cl$_2$]$^-$, in agreement with the well known behavior of the rhodium analogue.[20] This fast reaction with HCl explains why [Ir(CO)$_2$Cl]$_2$ could not be detected during the reductive carbonylation of IrCl$_3$ in ethanol where [Ir(CO)$_2$Cl$_2$]$^-$ was the only complex isolated.[4] It also explains the formation of minor amounts of [Ir(CO)$_2$Cl$_2$]$^-$ observed during the carbonylation of [Ir(COT)$_2$Cl]$_2$ on the silica surface since some HCl is generated during the reductive carbonylation to form [Ir$_4$(CO)$_{12}$]. [Ir(CO)$_2$(pyridine)Cl][19] is obtained quantitatively after a few minutes when pyridine is added at room temperature to an acetonitrile solution of [Ir(CO)$_2$Cl]$_2$. Similarly, [Ir(CO)$_2$(p-toluidine)-Cl][14,19,21] can be prepared by addition of p-toluidine to [Ir(CO)$_2$Cl]$_2$ in acetonitrile. When triphenylphosphine is added to an acetonitrile solution of [Ir(CO)$_2$Cl]$_2$ at room temperature, a yellow powder of [Ir(CO)(PPh$_3$)$_2$-Cl][19] precipitates. The reaction is complete in 15 min. Again, the reactivity of [Ir(CO)$_2$Cl]$_2$ is totally reminiscent of that of [Rh(CO)$_2$Cl]$_2$.[22]

The complex [Ir(CO)$_2$(acac)][15] is slowly formed along with [Ir(CO)$_2$Cl$_2$]Na[10] when acetylacetone and sodium bicarbonate are added under nitrogen to a solution of [Ir(CO)$_2$Cl]$_2$ in acetonitrile. The reaction is complete after 5 h. The products may be easily separated due to their different solubilities (see Experimental Section). When the reaction is carried out under reflux for 4 h, all [Ir(CO)$_2$Cl]$_2$ is converted to [Ir(CO)$_2$(acac)],[15] no [Ir-(CO)$_2$Cl$_2$]Na being observed under these conditions.

Conclusion

A pale-blue "Ir(CO)$_2$Cl" species (most probably [Ir-(CO)$_2$(HOSi≡)Cl] where the surface silanol groups act as ligands) is easily prepared on the silica surface by carbonylation of physisorbed [Ir(COT)$_2$Cl]$_2$ working at room temperature and atmospheric pressure. Prolonged treatment under the same conditions leads to [Ir$_4$(CO)$_{12}$], this reductive carbonylation being induced by water physisorbed on the silica surface, while at 100

°C [Ir(CO)$_3$Cl]$_n$ sublimes. The surface iridium dicarbonyl species can be extracted with donor solvating solvents, such as acetonitrile, affording a solution of [Ir-(CO)$_2$Cl]$_2$. A similar species may be produced directly in solvents like acetonitrile or acetone by reaction with CO at room temperature and atmospheric pressure. This kind of solvent is necessary to avoid polymerization of the [Ir(CO)$_2$Cl]$_2$ units to [Ir(CO)$_2$Cl]$_n$. To our knowledge, this is the first time that the dimeric species [Ir-(CO)$_2$Cl]$_2$ has been produced and characterized at least by mass spectroscopy. Attempts to isolate this dimer in the solid state failed, due to its quick polymerization via infinite Ir—Ir interactions to the corresponding black material [Ir(CO)$_2$Cl]$_n$. Work is in progress to determine the nature of the Ir—Ir interactions in this polymeric material and in the pale-blue [Ir(CO)$_2$(HOSi≡)Cl] surface species by EXAFS.

The acetonitrile solution of [Ir(CO)$_2$Cl]$_2$ is a very convenient starting material for the easy and high-yield synthesis of a series of Ir(I) carbonyl compounds, [Ir-(CO)$_3$Cl]$_n$, the traditional starting compound, is much less reactive, requiring usually higher temperatures and reaction times.

Experimental Section

General Comments. [Ir(COT)$_2$Cl]$_2$ was prepared according to the literature.[23] Silica (Aerosil 200 Degussa, with a nominal surface area of 200 m^2/g) was used as support. Solvents were dried over molecular sieves (4 Å) prior to use. Infrared spectra were recorded on a Nicolet MX-1 FT spectrometer, while a VG analytical 7070 EQ spectrometer was used for mass spectral determinations. Thermogravimetric analyses were run on a Perkin-Elmer thermogravimetric analyzer TGA 7. Elemental analyses were carried out at REDOX laboratories (Cologno Monzese, Milan, Italy).

Carbonylation of [Ir(COT)$_2$Cl]$_2$ Supported on Silica. As a Pressed Wafer. A silica wafer (0.060 g, 18 mm diameter) was fitted to a Pyrex support, which can slide inside an infrared cell of special design with CaF$_2$ windows; this cell allows measurements to be carried out under vacuum or a controlled atmosphere, as previously described.[24] The wafer was treated in air at 400 °C overnight, heated at 500 °C under high vacuum (10^{-5} Torr) for 7 h, and then allowed to cool under vacuum at room temperature. A saturated solution of [Ir-(COT)$_2$Cl]$_2$ in dehydrated dichloromethane (0.12 mL) was slowly dropped onto the wafer under a flow of argon. The yellow impregnated wafer was dried under high vacuum at room temperature and then exposed to CO at atmospheric pressure. The surface reactions were monitored by infrared spectroscopy (see Results and Discussion).

As a Powder. In the cylindrical Pyrex vessel previously described,[3] silica (2.99 g) was treated under high vacuum (10^{-5} Torr) for 16 h at 500 °C and then allowed to cool under vacuum at room temperature. [Ir(COT)$_2$Cl]$_2$ (0.139 g; 2% wt Ir/SiO$_2$) and dehydrated CH$_2$Cl$_2$ (100 mL) were added under nitrogen. The resultant slurry was stirred for 1 h, dried, left under high vacuum for 24 h, and then exposed to CO at room temperature and atmospheric pressure. The carbonylation was monitored by infrared spectroscopy; samples were taken from the glass vessel under nitrogen and studied as Nujol mulls. The surface iridium complex was extracted from the silica surface with dehydrated acetonitrile under nitrogen through a Pyrex Buchner filter funnel.

[Ir(CO)$_2$Cl]$_2$ in acetonitrile: IR ν(CO) 2085 (s), 2008 (s) cm^{-1}; MS ($T = 25$ °C; $I = 5.9$ V) m/e 568 [M]$^+$, 540 [M − CO], 512 [M

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− 2CO], 484 [M − 3CO], 456 [M − 4CO], 421 [M − 4CO − Cl], 386 [M − 4CO − 2Cl].

When [Ir(COT)$_2$Cl]$_2$ supported on silica was exposed to CO (1 atm) and heated at 100 °C, [Ir(CO)$_3$Cl]$_n$ sublimed on the cold part of the reaction vessel.

[Ir(CO)$_3$Cl]$_n$: IR (Nujol) ν(CO) 2079 (br, s), 2033 (w, sh) cm^{-1}; IR (Nujol) ν(Ir−Cl) 375 (w) cm^{-1};[9] MS (T = 25 °C; I = 5.9 V) m/e 312 [M]$^+$, 284 [M − CO], 256 [M − 2CO], 228 [M − 3CO], 193 [M − 3CO − Cl], peaks at 568, 540, 512, 484, 456, 421, and 386 are also present due to the formation of some [Ir-(CO)$_2$Cl]$_2$, probably during the vaporization of the sample.

Carbonylation of [Ir(COT)$_2$Cl]$_2$ in Solution. In Pentane or Toluene. [Ir(COT)$_2$Cl]$_2$ (0.145 g, 0.162 mmol) was added to dehydrated pentane or toluene (200 mL) in a three-necked flask under nitrogen, affording a yellow solution. As soon as nitrogen was replaced by CO, a carbonyliridium compound was formed, as shown by the appearance of two bands at 2081 and 2006 cm^{-1} in the infrared spectrum of the resulting yellow-green, almost blue, solution. Simultaneously, a dark almost black, powder began to precipitate. After 5 min, no carbonyliridium species was left in the colorless solution, as shown by infrared spectroscopy. The precipitate was separated by centrifugation (3000 RPM) and dried at 160 °C under nitrogen for 2 h, affording a black powder (0.090 g). Thermogravimetry, under nitrogen at a scanning rate of 3 °C/min, showed that the black powder undergoes a continuous weight loss of 34% from 160 to 550 °C. This weight loss would be in rather good agreement with the decomposition of a "Ir-(CO)$_2$Cl" unit to metallic iridium (calculated weight loss should be 32%).

Anal. Calcd for [Ir(CO)$_2$Cl]$_n$: C, 8.47; Cl, 12.50; O, 11.28. Found: C, 8.58; Cl, 12.89; O, 10.91. [Ir(CO)$_2$Cl]$_n$: IR (Nujol) ν(CO) 2088 (sh), 2076 (vbr, s), 2062 (sh) cm^{-1}; IR (Nujol) ν-(Ir−Cl) 327 (br, w) cm^{-1}; MS (T = 25 °C; I = 5.9 V) m/e 568 [M]$^+$ where M = [Ir(CO)$_2$Cl]$_2$, 540 [M − CO], 512 [M − 2CO], 484 [M − 3CO], 456 [M − 4CO], 421 [M − 4CO − Cl], 386 [M − 4CO − 2Cl].

In Acetonitrile. [Ir(COT)$_2$Cl]$_2$ (0.208 g, 0.232 mmol) did not dissolve in acetonitrile (50 mL) even after 30 min of stirring under nitrogen at room temperature. However, as soon as nitrogen was replaced by CO, a yellow solution was obtained. Its infrared spectrum showed the presence of [Ir(CO)$_2$Cl]$_2$ (ν-(CO) = 2085 (s) and 2008 (s) cm^{-1} in acetonitrile; see Results and Discussion).

Evaporation of the acetonitrile at room temperature afforded a dark-brown solid material whose infrared spectrum, taken as a Nujol mull, was characterized by ν(CO) at 2111 (sh), 2086 (vbr, s), and 2060 (sh) cm^{-1} and by ν(Ir−Cl) at 327 (br, w) cm^{-1}. This material was not pure [Ir(CO)$_2$Cl]$_n$ but still contained acetonitrile, as shown by elemental and thermogravimetric analyses and by ^{1}H NMR spectroscopy (carried out by dissolving the dark material in CD$_3$OD). Acetonitrile could be completely removed by treatment under a flow of nitrogen at 180 °C for about 3 h. The thermogravimetric analysis and the infrared spectrum of the resulting black material were similar to those of [Ir(CO)$_2$Cl]$_n$ prepared by carbonylation of [Ir-(COT)$_2$Cl]$_2$ in pentane, as described above.

Synthesis of [Ir(CO)$_2$Cl$_2$][PPN]. In a three-necked flask [Ir(COT)$_2$Cl]$_2$ (0.051 g, 0.057 mmol) was added to dehydrated CH$_3$CN (30 mL) under nitrogen. The suspension was stirred for 2 min, and then nitrogen was replaced by CO. Undissolved [Ir(COT)$_2$Cl]$_2$ disappeared immediately, and a yellow solution was obtained. After 2 min under CO, [PPN]Cl (0.065 g, 0.113 mmol) was added. After 2 min, all the [Ir(CO)$_2$Cl]$_2$ species had been converted to [Ir(CO)$_2$Cl$_2$][PPN], as shown by infrared spectroscopy. Evaporation of the solvent afforded [Ir(CO)$_2$-Cl$_2$][PPN][10] (0.094 g, 0.110 mmol; 97% yield).

[Ir(CO)$_2$Cl$_2$][PPN]: IR (in acetonitrile) ν(CO) 2055 (s), 1972 (s) cm^{-1}.

Synthesis of [Ir(CO)$_2$(pyridine)Cl] and [Ir(CO)$_2$(p-toluidine)Cl]. In a three-necked flask [Ir(COT)$_2$Cl]$_2$ (0.051 g, 0.057 mmol) was added to dehydrated CH$_3$CN (30 mL) under nitrogen. The suspension was stirred for 2 min, and then nitrogen was replaced by CO. Undissolved [Ir(COT)$_2$Cl]$_2$ disappeared immediately, and a yellow solution was obtained. After 2 min under CO, pyridine (0.2 mL) or p-toluidine (0.012 g) was added. After 5 min, all [Ir(CO)$_2$Cl]$_2$ had been converted in [Ir(CO)$_2$(pyridine)Cl] or [Ir(CO)$_2$(p-toluidine)Cl], respectively, as shown by infrared spectroscopy. Evaporation of the solvent gave [Ir(CO)$_2$(pyridine)Cl][19] (0.041 g, 0.113 mmol; 99% yield) or [Ir(CO)$_2$(p-toluidine)Cl][14,19,21] (0.042 g, 0.107 mmol; 94% yield after recrystallization from benzene/pentane).

[Ir(CO)$_2$(pyridine)Cl]: IR (in acetonitrile) ν(CO) 2077 (s), 1996 (s) cm^{-1}; IR (as KBr) ν(CO) 2072 (s), 1998 (s) cm^{-1};[19] MS (T = 25 °C; I = 7.6 V) m/e 363 [M]$^+$, 335 [M − CO], 307 [M − 2CO], 271 [M − 2CO − Cl], 193 [M − 2CO − Cl − pyridine], peaks at 568, 540, 512, 484, 456, 421, and 386 are also present due to the formation of some [Ir(CO)$_2$Cl]$_2$, probably during the vaporization of the sample.

[Ir(CO)$_2$(p-toluidine)Cl]: IR (in acetonitrile) ν(CO) 2075 (s), 1993 (s) cm^{-1}; IR (as Nujol) ν(CO) 2088 (s), 2027 (s) cm^{-1}.[21]

Synthesis of [Ir(CO)(PPh$_3$)$_2$Cl]. In a three-necked flask [Ir(COT)$_2$Cl]$_2$ (0.051 g, 0.057 mmol) was added to dehydrated CH$_3$CN (30 mL) under nitrogen. The suspension was stirred for 15 min, and then nitrogen was replaced by CO. Undissolved [Ir(COT)$_2$Cl]$_2$ disappeared immediately, and a yellow solution was obtained. After 5 min under CO, triphenylphosphine (0.065 g, 0.249 mmol), which is soluble in acetonitrile, was added. Almost immediately, yellow [Ir(CO)(PPh$_3$)$_2$Cl] began to precipitate. After 15 min the reaction was complete, as shown by infrared spectroscopy. After filtration, the precipitate was washed with a few milliliters of CH$_3$CN, affording [Ir(CO)(PPh$_3$)$_2$Cl][19] (0.085 g, 0.109 mmol; 96% yield): IR (in dichloromethane) ν(CO) 1964 cm^{-1};[19] MS m/e 779 [M]$^+$, 751 [M − CO], 716 [M − CO − Cl].

Synthesis of [Ir(CO)$_2$(acac)]. In a three-necked flask [Ir-(COT)$_2$Cl]$_2$ (0.070 g, 0.078 mmol) was added to dehydrated CH$_3$CN (40 mL) under nitrogen. The suspension was stirred for 2 min, and then nitrogen was replaced by CO. After 2 min under CO, pentane-2,4-dione (0.5 mL) and excess NaHCO$_3$ (0.50 g) were added. The suspension was stirred under nitrogen at room temperature. [Ir(CO)$_2$(acac)][15] and [Ir-(CO)$_2$Cl$_2$]Na[10] were slowly formed as shown by infrared spectroscopy. The reaction was complete after 5 h. Filtration of the reaction mixture, followed by evaporation of the solvent afforded a brown residue. This was extracted with hot hexane (30 mL). [Ir(CO)$_2$Cl$_2$]Na did not dissolve in hexane and was thus separated by filtration (0.022 g, 0.064 mmol; 43% yield). Besides, the hexane solution was concentrated and cooled to give yellow golden crystals of [Ir(CO)$_2$(acac)] (0.027 g, 0.078 mmol; 50% yield). When the reaction was carried out under reflux for 4 h, all [Ir(CO)$_2$Cl]$_2$ was converted to [Ir(CO)$_2$-(acac)].[15]

[Ir(CO)$_2$(acac)]: IR (in acetonitrile) ν(CO) 2073 (s), 1996 (s) cm^{-1}.

[Ir(CO)$_2$Cl$_2$]Na: IR (in acetonitrile) ν(CO) 2055 (s), 1972 (s) cm^{-1}.