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Surface organometallic chemistry: the easy conversion of $[Ir_6(CO)_{16}]$ supported on silica into $[Ir_4(CO)_{12}]$ [☆]

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Abstract

$[Ir_6(CO)_{16}]$ is deposited on silica from a solution as large crystallites. By heating under Ar at 100°C, a disaggregation of the crystallites occurs followed by conversion of the original $[Ir_6(CO)_{16}]$ cluster to $[Ir_4(CO)_{12}]$ and metal particles covered by CO. Treatment of these metal particles first with O_2 and then with CO at 100°C affords $[Ir_4(CO)_{12}]$, thus allowing a high conversion of $[Ir_6(CO)_{16}]$ into $[Ir_4(CO)_{12}]$. More directly, $[Ir_6(CO)_{16}]$ supported on silica may be converted to $[Ir_4(CO)_{12}]$ by successive treatments under O_2 and CO at 100°C. The formation of $[Ir_4(CO)_{12}]$ from $[Ir_6(CO)_{16}]$ supported on silica is inhibited by CO.

Keywords: Iridium; Carbonyl clusters; Supported clusters

1. Introduction

There has been considerable interest in recent years in the reactivity of organometallic complexes with surfaces of metal oxides. A large amount of work has been devoted to the chemical behaviour of metal carbonyls of various nuclearities supported on metal oxides such as silica, alumina and magnesia [1–6]. These studies have revealed a great variety of surface reactions with the functional groups of the metal oxides surface (i.e. acid–base OH groups, Lewis basic site O^{2-} and Lewis acidic sites Al^{3+} and Mg^{2+}).

There are several reports on the surface organometallic chemistry of $[Ir_4(CO)_{12}]$ supported on inorganic oxides [7–16]. On partially dehydroxylated MgO, $[Ir_4(CO)_{12}]$ is converted to $[HIr_4(CO)_{11}]^-$ at room temperature [7]. The preparation of very dispersed metallic iridium particles by thermal decomposition of $[Ir_4(CO)_{12}]$ supported on alumina [8,9] or silica [9–16] is well documented. The physisorption and redispersion of $[Ir_4(CO)_{12}]$ on the silica surface by mild thermal treatment have also been described [14–16].

Although the behaviour of $[Ir_4(CO)_{12}]$ supported on inorganic oxides has been the subject of many investigations, to our knowledge, that of $[Ir_6(CO)_{16}]$ has not yet been reported.

Here we report our investigation on the behaviour of $[Ir_6(CO)_{16}]$ supported on the silica surface, together with evidence for cluster breakdown from Ir_6 to Ir_4 clusters under mild conditions.

2. Results and discussion

2.1. Physisorption of $[Ir_6(CO)_{16}]$ on the silica surface

When the isomer of $[Ir_6(CO)_{16}]$ with four face-bridging carbonyl [17], characterized by a bridging carbonyl band at 1764 cm^{-1} (KCl pellet), is dissolved in dichloromethane, a mixture of the isomers with four face-bridging carbonyl (bridging $\nu(CO)$ = 1780(w) cm^{-1}) and with four edge-bridging carbonyl [17] (bridging $\nu(CO)$ = 1842(w) cm^{-1}) is obtained (Fig. 1a).

When this dichloromethane solution of $[Ir_6(CO)_{16}]$ is stirred with silica under Ar at room temperature overnight and then dried under vacuum, a pale-orange powder is obtained. The IR spectrum of a wafer prepared with this powder (Fig. 1b) shows a bridging carbonyl absorption at 1763(s) cm^{-1} and terminal car-

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[☆] Dedicated to Professor Fausto Calderazzo in recognition of his important contributions to organometallic chemistry.

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bonyl absorptions at 2117(w), 2086(sh), 2077(sh), 2068(s), 2057(sh), 2049(m), 2037(m), 2016(w) and 2010(m) cm^{-1}. Two negative absorptions also appear, at 2132 and 1808 cm^{-1}, owing to some Christiansen effect [18]. This spectrum is very similar to that of the isomer of [$Ir_6(CO)_{16}$] with four face-bridging carbonyl ligands as KCl pellet (Fig. 1c). There is no bridging carbonyl band at around 1842 cm^{-1}, suggesting that during the impregnation process the isomer of [$Ir_6(CO)_{16}$] with four edge-bridging carbonyl ligands, which is present in the dichloromethane solution (Fig. 1a), has been converted to the isomer with four face-bridging carbonyl ligands, physisorbed on the silica surface. This behaviour is not surprising since evaporation of a solution of the [$Ir_6(CO)_{16}$] isomers leads to the complete conversion of the isomer with four edge-bridging carbonyl ligands to that with four face-bridging carbonyl ligands (Fig. 1c) [19]. Also simple physisorption of [$Ir_6(CO)_{16}$] on the silica surface is confirmed by its easy extraction with dichloromethane.

However, when a wafer of silica is impregnated with a dichloromethane solution containing the two [$Ir_6(CO)_{16}$] isomers, the IR spectrum of the resulting wafer (Fig. 1d) is somewhat different from that observed for a wafer obtained by pressing a powder sample of [$Ir_6(CO)_{16}$] supported on silica, especially in the bridging carbonyl region (compare d and b Fig. 1). There is an absorption at 1831(m) cm^{-1} in addition to that at 1763(m) cm^{-1} (Fig. 1d). These data suggest that both [$Ir_6(CO)_{16}$] isomers remain on the silica surface owing to the rapid evaporation of the solvent.

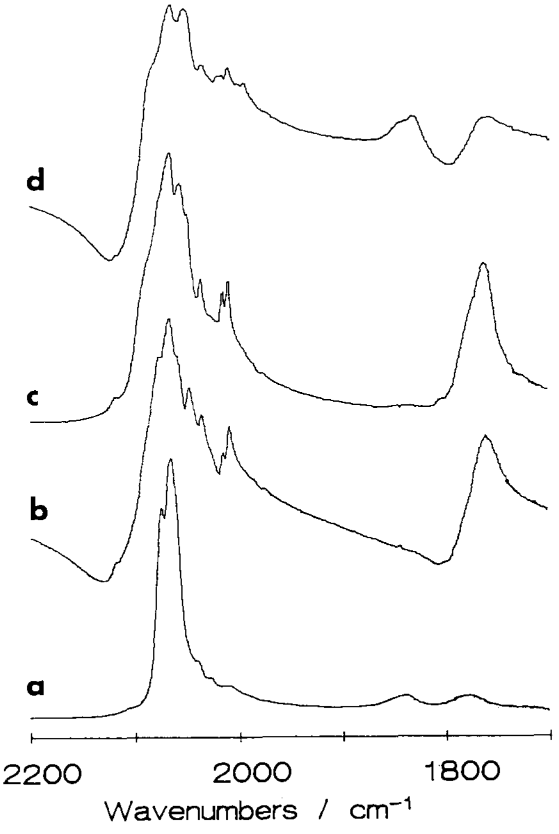


Fig. 1. Physisorption of [$Ir_6(CO)_{16}$] on the silica surface, as shown by IR spectra in the ν(CO) region: (a) CH_2Cl_2 solution of a mixture of the isomers of [$Ir_6(CO)_{16}$] with four face-bridging and four edge-bridging carbonyl ligands respectively; (b) physisorbed [$Ir_6(CO)_{16}$] on SiO_2 powder, subsequently pressed as wafer; (c) isomer of [$Ir_6(CO)_{16}$] with four face-bridging carbonyl ligands, as KCl pellet; (d) physisorbed [$Ir_6(CO)_{16}$] on SiO_2 wafer.

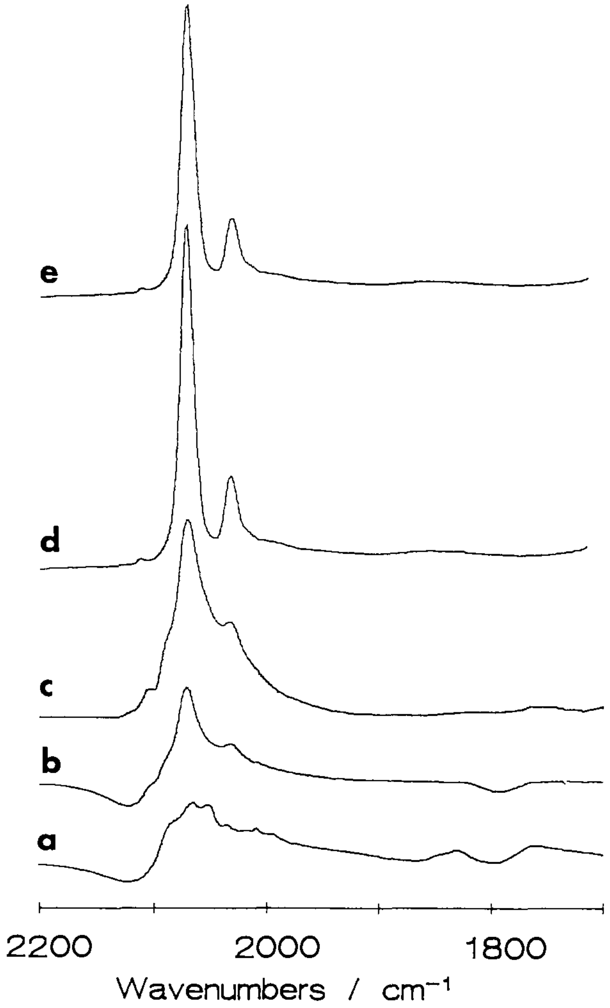


Fig. 2. Reactivity of [$Ir_6(CO)_{16}$] supported on SiO_2 wafer under Ar, as shown by IR spectra in the ν(CO) region: (a) physisorbed [$Ir_6(CO)_{16}$] on SiO_2; (b) after 3 h at 100°C under Ar; (c) after additional 66 h at 100°C under Ar; (d) [$Ir_4(CO)_{12}$] molecularly dispersed on SiO_2; (e) (c) after successive 3 h at 100°C under O_2 and 68 h at 100°C under CO.

The Christiansen effect observed in the IR spectra of silica-supported [$Ir_6(CO)_{16}$] (powder or wafer samples) indicates that this cluster, like [$Ir_4(CO)_{12}$] [16], is deposited as large crystallites on the silica surface.

2.2. *Reactivity of [$Ir_6(CO)_{16}$] supported on silica*

[$Ir_6(CO)_{16}$] physisorbed on a wafer of silica is stable under Ar at room temperature (Fig. 2a). However, treatment at 100°C for only 3 h produces changes as shown by the resultant IR spectrum characterized by two carbonyl bands at 2072(s) and 2032(m) cm^{-1} (Fig. 2b). The negative absorptions due to some residual [$Ir_6(CO)_{16}$] crystallites may be completely removed by further treatment at 100°C under Ar for 66 h (Fig. 2c). The resulting IR spectrum is reminiscent of that of molecularly dispersed [$Ir_4(CO)_{12}$] supported on silica (Fig. 2d) [16]. However, the carbonyl bands are less narrow, suggesting that there is another carbonyl species in addition to [$Ir_4(CO)_{12}$]. (In fact, subtraction of the IR spectrum of pure [$Ir_4(CO)_{12}$] supported on silica from Fig. 2c affords a broad band centred at 2065 cm^{-1}.)

Thus, in order to investigate the nature of the carbonyl species formed together with [$Ir_4(CO)_{12}$] (Fig. 3a), the molecularly dispersed [$Ir_4(CO)_{12}$] was eliminated from the silica surface by further treatment of the wafer under vacuum at 100°C and 150°C for 19 h and 5 h respectively, monitoring the disappearance of the bands at 2072(s) and 2032(m) cm^{-1}. The thermal treatment causes a frequency shift of the residual broad carbonyl absorption from 2065 cm^{-1} (Fig. 3b) to 2020 cm^{-1} (Fig. 3c). Exposure to CO at room temperature shifts the carbonyl absorption at 2055 cm^{-1} (Fig. 3d) while treatment under CO at 150°C for 23 h causes a further shift at 2065 cm^{-1} (Fig. 3e). This kind of IR shift due to the decarbonylation–recarbonylation process is typical of metallic particles of iridium [20,21].

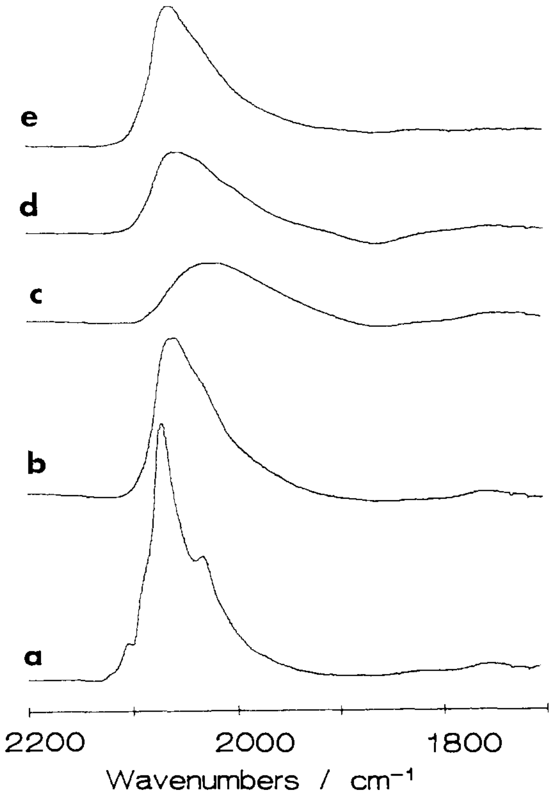
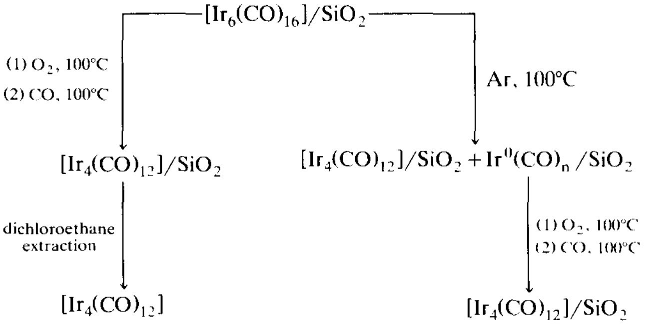


Fig. 3. IR spectra in the ν(CO) region: (a) physisorbed [$Ir_6(CO)_{16}$] on SiO_2 after 69 h at 100°C under Ar; (b) after treatment under vacuum at 100°C for 19 h; (c) after additional treatment under vacuum at 150°C for 5 h; (d) after 89 h under CO at room temperature; (e) after additional 23 h at 150°C under CO.



Scheme 1.

These results suggest that even rather mild thermal treatment under Ar of [$Ir_6(CO)_{16}$] supported on silica causes progressive disrupture of the initial large aggregates of [$Ir_6(CO)_{16}$] crystallites, as indicated by the disappearance of the Christiansen effect. Simultaneously, molecularly dispersed [$Ir_4(CO)_{12}$] is formed, together with metallic particles of iridium covered by CO (Scheme 1).

Consistent with the literature data [16], these metallic iridium particles are completely decarbonylated under O_2 either at room temperature or more rapidly at 100°C, and further exposure to CO at 100°C affords molecularly dispersed [$Ir_4(CO)_{12}$].

Thus treatment under dioxygen of the mixture of molecularly dispersed [$Ir_4(CO)_{12}$] and metallic particles (Fig. 2c) followed by admission of CO at 100°C causes an increase in the intensity of the carbonyl bands at 2072 and 2032 cm^{-1} and gives a clean spectrum of molecularly dispersed [$Ir_4(CO)_{12}$] (Fig. 2e).

To evaluate quantitatively the conversion on the surface of [$Ir_6(CO)_{16}$] to [$Ir_4(CO)_{12}$], we investigated the reactivity of [$Ir_6(CO)_{16}$] supported on silica as powder. After treatment under Ar at 100°C for 48 h, the breakdown of [$Ir_6(CO)_{16}$] was complete as shown by IR spectroscopy. Extraction with hot dichloroethane afforded [$Ir_4(CO)_{12}$] (52% of the initial iridium content had been converted to [$Ir_4(CO)_{12}$], a 78% yield, assuming that 1 mol of [$Ir_6(CO)_{16}$] should give 1 mol of [$Ir_4(CO)_{12}$]). The remaining supported metallic iridium was heated at 100°C first under O_2 and then under CO for 1 and 48 h respectively. Extraction with hot dichloroethane afforded more [$Ir_4(CO)_{12}$] (an additional 31% of the initial iridium content had been converted to [$Ir_4(CO)_{12}$]; global yield of 83%, assuming that 1 mol of [$Ir_6(CO)_{16}$] should give 1.5 mol of [$Ir_4(CO)_{12}$]).

The reactivity of [$Ir_6(CO)_{16}$] supported on silica was investigated under dioxygen. [$Ir_6(CO)_{16}$] physisorbed on a wafer of silica is stable under O_2 at room temper-

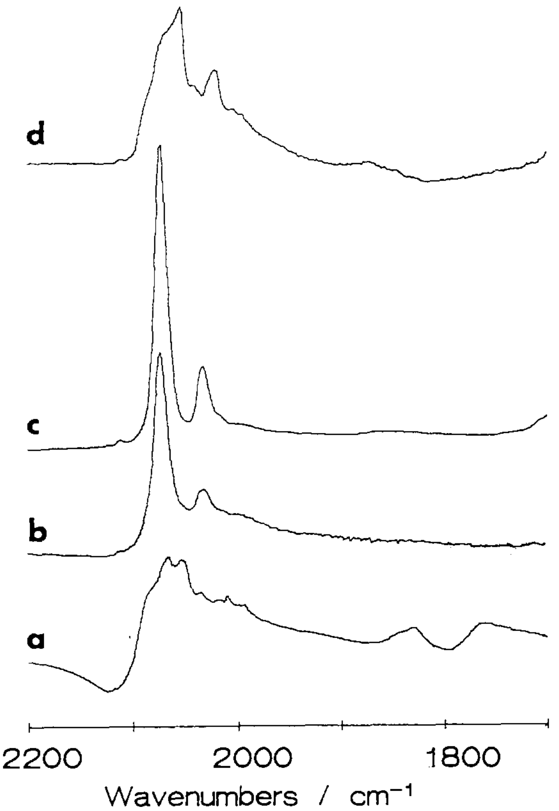


Fig. 4. Reactivity of $[Ir_6(CO)_{16}]$ supported on SiO_2 wafer under O_2, as shown by IR spectra in the $\nu(CO)$ region: (a) physisorbed $[Ir_6(CO)_{16}]$ on SiO_2 after 24 h at 25°C under O_2; (b) after further 7 h at 100°C under O_2; (c) after further exposure to CO at 100°C for 20 h; (d) after further exposure to H_2O vapour for 24 h at 25°C and successive outgassing for 10 min.

ature, for at least 24 h (Fig. 4a). By heating to 100°C for only 7 h, the negative absorptions due to $[Ir_6(CO)_{16}]$ crystallites disappear and a clean spectrum of well-dispersed $[Ir_4(CO)_{12}]$ is obtained (Fig. 4b). The broad absorption typical of metallic iridium covered by CO is not observed, because the iridium particles are covered by a layer of oxygen under these reaction conditions [16]. The pair of bands at 2072(s) and 2032(m) cm^{-1} becomes more intense when the wafer is exposed to CO at 100°C for 20 h (Fig. 4c), consistent with easy conversion of the iridium particles covered by O_2 into $[Ir_4(CO)_{12}]$ [16]. Further treatment with water vapour causes an aggregation of the well-dispersed $[Ir_4(CO)_{12}]$ molecules to form small crystallites [16], as shown by the resultant IR spectrum (Fig. 4d).

During our study on the reactivity of $[Ir_6(CO)_{16}]$ supported on silica under O_2, we never detect the formation of $Ir^{I}(CO)_2$ species anchored to the silica surface, which should be characterized by a pair of carbonyl bands at 2080(s) and 2008(s) cm^{-1} [9]. Thus, as we have already reported [16], the oxidation of iridium clusters does not occur easily on the silica surface, although it occurs readily on alumina [9,21].

The reactivity of $[Ir_6(CO)_{16}]$ physisorbed on silica powder was similar to that observed on silica wafers (Scheme 1). After successive treatments at 100°C under O_2 and under CO for 2 and 48 h respectively, extraction with hot dichloroethane affords $[Ir_4(CO)_{12}]$ (81% yield, assuming that 1 mol of $[Ir_6(CO)_{16}]$ should give 1.5 mol of $[Ir_4(CO)_{12}]$).

Owing to the absence of any strong chemical interactions with $[Ir_6(CO)_{16}]$, the silica surface may be considered as a solid neutral reaction medium.

The conversion of $[Ir_6(CO)_{16}]$ to $[Ir_4(CO)_{12}]$ under mild conditions is an unexpected surface process because an increase in cluster nuclearity on thermal treatment would be expected. For example, silica-physisorbed $[Rh_6(CO)_{16}]$ is easily obtained even by vacuum treatment of $[Rh_4(CO)_{12}]$ [22]. However, in solution, some breakdown reactions of ruthenium and osmium clusters have been reported but that is under relatively high pressures of CO and H_2 [23].

The direct solid state conversion of $[Ir_6(CO)_{16}]$ to $[Ir_4(CO)_{12}]$ would require CO. However, when physisorbed $[Ir_6(CO)_{16}]$ was heated at 100°C under CO for 24 h, no reaction occurred, as shown by IR spectroscopy. Extraction with dichloromethane afforded pure $[Ir_6(CO)_{16}]$, suggesting that this cluster supported on the silica surface is stabilized under CO. Most probably the presence of CO inhibits the break-up of the $[Ir_6(CO)_{16}]$ metal cage. In addition, once formed, $[Ir_4(CO)_{12}]$ supported on silica is also stable under CO at 100°C. It does not react further to give $[Ir_6(CO)_{16}]$ or metal particles. This is different from that which is observed in zeolite cages where $[Ir_4(CO)_{12}]$ is converted to $[Ir_6(CO)_{16}]$ by treatment with CO at 125°C [24]. It has also been reported that, on the basic surface of MgO, $[Ir_4(CO)_{12}]$ easily increases its nuclearity to give anionic $[Ir_6(CO)_{15}]^{2-}$ [7]. This is expected because it is known that, in basic solution, $[Ir_6(CO)_{16}]$ gives readily $[Ir_6(CO)_{15}]^{2-}$ [17] while $[Ir_4(CO)_{12}]$ affords mixtures of $[Ir_6(CO)_{15}]^{2-}$ and $[Ir_8(CO)_{22}]^{2-}$ [25]. Thus the observed decrease in nuclearity from $[Ir_6(CO)_{16}]$ to $[Ir_4(CO)_{12}]$ on the silica surface must be explained by the very high stability of $[Ir_4(CO)_{12}]$ in a neutral reaction medium. Studies of the thermal behaviour of $[Ir_6(CO)_{16}]$ in non-basic solutions are in progress to determine whether stabilization of $[Ir_4(CO)_{12}]$ occurs [19] under solvation conditions similar to those expected on the silica surface.

3. Conclusion

$[Ir_6(CO)_{16}]$, like $[Ir_4(CO)_{12}]$, does not interact strongly with the silica surface, either by anchoring through covalent bonding or by oxidative break-up of the metal cage. The silica surface may thus be considered as a neutral solid reaction medium, where crystallites of $[Ir_6(CO)_{16}]$ are initially deposited. Mild thermal treatment under Ar leads to a disaggregation of these crystallites, followed by decomposition to metallic iridium and [$Ir_4(CO)_{12}$] evenly distributed on the surface. This molecular surface cluster breakdown process, which occurs in the absence of CO, is quite an unusual reaction in the chemistry of metal carbonyl clusters.

4. Experimental details

4.1. Starting materials and instrumentation

[$Ir_6(CO)_{16}$] was prepared according to the literature [25]. Aerosil 200 Degussa, with a nominal surface area of 200 m^2 g^{-1}, was used as support. The supported samples were prepared by solvent impregnation of silica as powder and as pressed wafers. IR spectra were obtained by use of a Nicolet 10-DX Fourier transform spectrophotometer, with a resolution of 4 cm^{-1}. In all cases the background spectrum of pure silica was subtracted.

4.2. Preparation and reactivity of pressed wafer samples

Silica (60 mg) was pressed as a wafer (18 mm diameter) and fitted to a Pyrex support which can slide inside an IR cell with CaF_2 windows of special design, which can work under vacuum or a controlled atmosphere as previously described [26]. A saturated solution of [$Ir_6(CO)_{16}$] in anhydrous dichloromethane was added slowly to the silica under a flow of Ar. The resulting wafer was then dried under high vacuum (10^{-5} Torr) at room temperature.

The cell containing [$Ir_6(CO)_{16}$] physisorbed on a silica wafer was put under Ar or O_2 and heated to temperatures between 25 and 100°C. The surface reactions were followed by IR spectroscopy.

4.3. Preparation and reactivity of powder samples

In a typical experiment, a mixture of silica (14.76 g), [$Ir_6(CO)_{16}$] (204 mg; 1% by weight Ir/SiO_2) and dehydrated dichloromethane (300 ml) was stirred overnight at room temperature under Ar. The resulting orange slurry was dried under vacuum (10^{-2} Torr) affording a pale-orange powder which was stored under Ar.

4.3.1. Reactivity under Ar

The powder sample containing physisorbed [$Ir_6(CO)_{16}$] (5.670 g of powder sample; 0.0774 g of [$Ir_6(CO)_{16}$]; 0.0483 mmol of [$Ir_6(CO)_{16}$]) was put in a glass vessel equipped with Teflon stopcocks, which can work in vacuum or a controlled atmosphere, as previously described [27], and treated with Ar (300 Torr) at 100°C for 48 h. The resulting powder was extracted with hot dichloroethane (300 ml; under reflux for 4 h). Evaporation of the dichloroethane solution gave [$Ir_4(CO)_{12}$], identified by IR and mass spectroscopy (42 mg; 0.038 mmol; 78% yield assuming that 1 mol of [$Ir_6(CO)_{16}$] is converted to 1 mol of [$Ir_4(CO)_{12}$]). The remaining silica powder was treated at 100°C first with O_2 (300 Torr) and then with CO (760 Torr) for 1 and 48 h respectively. Extraction with dichloroethane (150 ml; 4 h under reflux) afforded [$Ir_4(CO)_{12}$] (25 mg; 0.023 mmol). The global yield was 83%, assuming that 1 mol of [$Ir_6(CO)_{16}$] is converted to 1.5 mol of [$Ir_4(CO)_{12}$].

4.3.2. Reactivity under O_2

A powder sample containing physisorbed [$Ir_6(CO)_{16}$] (3.850 g of powder sample; 0.0525 g of [$Ir_6(CO)_{16}$]; 0.0328 mmol [$Ir_6(CO)_{16}$]) was put in a glass vessel and treated at 100°C first with O_2 (300 Torr) and then with CO (760 Torr) for 2 and 48 h respectively. Extraction with hot dichloroethane (300 ml; under reflux for 4 h) gave yellow [$Ir_4(CO)_{12}$] (44 mg; 0.040 mmol; 81% yield, assuming that 1 mol of [$Ir_6(CO)_{16}$] gives 1.5 mol of [$Ir_4(CO)_{12}$]).

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