Solid-Gas Reactions of the "Lightly Stabilized" $Os_3(CO)_{11}L$ (L = NCCH₃, C₂H₄) Clusters with CO, NH₃, and H_2

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The solid-gas reactions of the "lightly stabilized" $Os_3(CO)_{11}L$ (L = NCCH₃ (1), L = C₂H₄ (2)) clusters with gaseous reactants as CO, NH_3 , and H_2 have been investigated. At 80 °C polycrystalline samples (ca. 50 mg) of 1 and 2 undergo substitution of the axially bound acetonitrile ligand and the equatorially coordinated ethene ligand by the gaseous reactants. 1 and 2 react with ${}^{13}CO$ to form $Os_3(CO)_{11}({}^{13}CO)$ (3a), but no site selectivity is observed for the labeled carbonyl ligand (as shown by ^{13}C MAS NMR). On reaction with NH₃ both 1 and 2 afford $Os_3(CO)_{11}(NH_3)$ (4) with the ammonia ligand coordinated in an axial position. The observed stereochemistry of the reaction products of 1 and 2 with CO and NH_3 suggests the presence of an unsaturated intermediate $Os_3(CO)_{11}$, which displays an intramolecular axialequatorial exchange of the vacant coordination site. Reaction with dihydrogen of solid Os₃- $(CO)_{11}(NCCH_3)$ (1) or $Os_3(CO)_{11}(C_2H_4)$ (2) gives $H_2Os_3(CO)_{11}$ as first product, which under the experimental conditions affords $Os_3(CO)_{12}$ and $H_2Os_3(CO)_{10}$.

Introduction

The development of solid-gas reactions¹⁻⁶ is of great interest not only for the positive ecological impact associated with the possibility of avoiding the use of organic solvents. As far as possible applications are concerned, a better knowledge of solid-gas reactions may provide useful insights into the design of novel sensor devices for gases. Furthermore, the investigation of stoichiometric transformations of organometallic solids may lead to the development of catalytic reactions in the solid state; this would be a viable alternative to heterogeneous catalysis using organometallic compounds supported on inorganic surfaces.

For a solid-gas reaction two general pathways can be envisaged: (a) The crystalline solid is loosely packed and contains channels through which small gaseous molecules can diffuse and flood the whole solid. (b) The gaseous molecules react at the surface of the solid disrupting the crystalline order and allowing more gaseous reactant to penetrate the interlayer spaces and interact with further substrate molecules. To get bulk reactivity, such a process may require the sliding of the product species over the surface of the solid; this step should be favored by an increase in temperature.

In principle, for organometallic compounds one would expect solid-gas reactions to take place readily if the solid substrate is coordinatively unsaturated. This has recently been shown⁷ by the solid state reactions of H_{2} - $Os_3(CO)_{10}$ (46 e⁻) with gaseous Lewis bases L (L = CO, NH₃, H₂S) which give rise to the electron precise adducts $H_2Os_3(CO)_{10}L$ (48 e⁻). We are interested in extending this approach through the use of organometallic compounds which may easily afford coordinatively unsaturated species upon spontaneous release of coordinated groups. Metal carbonyl clusters containing nitrile or olefin ligands as leaving groups have been shown to be very reactive $^{8-10}$ in solution, and for this reason, these derivatives are sometimes denoted as "lightly stabilized" systems.

In order to assess if these systems are also reactive in the solid state, we have studied the reactions between solid $Os_3(CO)_{11}L$ (L = NCCH₃, C_2H_4) clusters and gaseous reactants such as CO, NH_3 , and H_2 .

Results and Discussion

Reactions of Os₃(CO)₁₁(NCCH₃) (1) and Os₃(CO)₁₁- (C_2H_4) (2) with Carbon Monoxide. When crystalline yellow $Os_3(CO)_{11}(NCCH_3)$ (1) is reacted with CO (1 atm) at 80 °C, a pale yellow powder of $Os_3(CO)_{12}$ (3) is formed. The conversion is complete after several hours (12-24)h) as can be shown by IR. When 1 is reacted under the same conditions with ¹³CO (Scheme 1), Os₃(CO)₁₁(¹³CO) (3a) is obtained. The ¹³C MAS NMR spectrum of 3a shows that the ¹³CO ligand is equally distributed over axial (ax) and equatorial (eq) sites as shown by integra-

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Figure 1. ¹³C MAS spectrum (isotropic region only) of $Os_3(CO)_{11}(^{13}CO)$ (3a) obtained by the solid-gas reaction of 1 with ¹³CO. Experimental conditions: spinning speed 6000 Hz, recycle time 120 s, pulse width 1 μ s (20° pulse), ambient temperature.



tion of the relative areas of the two regions previously assigned to axial (from 188 to 180 ppm) and equatorial (from 175 to 167 ppm) carbonyls, respectively (Figure 1). Like 1, $Os_3(CO)_{11}(C_2H_4)$ (2) reacts with CO at 80 °C to form $Os_3(CO)_{12}$ (3). The reaction of 2 with ¹³CO affords Os₃(CO)₁₁(¹³CO) (3a) (Scheme 1), the ¹³C MAS NMR spectrum of which is equal to the spectrum shown in Figure 1. The observed minor line broadening of the 13 C resonances of **3a** with respect to the published spectrum of $Os_3(CO)_{12}$ ¹¹ appears to be associated with the powdery nature (microcrystals) of the product.

In principle, if a dissociative pathway for the reaction mechanism is assumed,¹² the axial coordination site of the acetonitrile ligand¹³ in 1 and the equatorial coordination site of the ethene ligand¹⁴ in 2 should confer an axial or equatorial site specificity, respectively, on the substitution product. Since solid $Os_3(CO)_{12}$ does not show any intermolecular exchange with ^{13}CO (80 °C, 24 h), the observed equal distribution of ¹³CO over axial

and equatorial sites indicates that fluxional behavior occurs at some stage during the reaction. Three possible fluxional processes may be taken into consideration: (1) a fluxionality at the $Os(CO)_3L$ (L = NCCH₃, C₂H₄) unit in the starting material (1, 2) preceding the release of the acetonitrile/ethene ligand; (2) an axial-equatorial CO rearrangement in $Os_3(CO)_{12}$; (3) a fluxional behavior involving the vacant site of the $Os(CO)_3$ unit in the postulated reaction intermediate $Os_3(CO)_{11}$.

Although ax-eq CO exchange in 1 and 2 (process 1) is known to occur in solution, VT-¹³C CPMAS spectroscopy over the temperature range 25-80 °C has shown that the solid compounds are rigid on the NMR time scale. A fast (NMR detectable) ax-eq CO exchange in solid $Os_3(CO)_{12}$ (process 2) can be ruled out since no line broadening is observed in the ¹³C MAS spectra of Os₃- $(CO)_{12}$ upon raising the temperature (spectra were recorded up to 120 °C).

However, complete scrambling of ¹³CO could also be achieved by a slow ax-eq CO exchange during the long reaction times necessary for complete conversion. Therefore, the reactions of 1 and 2 with 13 CO were interrupted after shorter reaction times (e.g. 2 h, corresponding to ca. 40% conversion) and the products were analyzed by ¹³C MAS NMR. In both cases equal distribution of ¹³CO over axial and equatorial sites was observed already at such early stages of the reaction. On the basis of these results, also a slow ax-eq rearrangement in $Os_3(CO)_{12}$ does not seem to be responsible for the observed equilibration of ¹³CO at ax and eq sites. Although there is still the possibility of a rearrangement process having an intermediate rate, we think that it is more likely that the lack of site specificity in the solid state reactions of both 1 and 2 with 13 CO is due to a fluxionality of the common unsaturated $Os_3(CO)_{11}$ intermediate (process 3): the vacant coordination site exchanges between axial and equatorial positions both of which are trapped by reaction with ¹³CO to yield the isoenergetical ax- and $eq-({}^{13}CO)Os_3(CO)_{11}$ in a 1:1 ratio.

The species $Os_3(CO)_{11}$ has already been observed by Wrighton et al.¹⁵ in a hydrocarbon glass at $T \le 110$ K as the product of photochemically induced loss of CO by $Os_3(CO)_{12}$. For $Os_3(CO)_{11}$ a rearrangement of the vacant coordination site from an equatorial to an axial position has been found, although no fluxional behavior was observed under the applied experimental conditions.

In order to further investigate the solid-gas reaction mechanism, we have studied the reaction of 1 and 2 with a gaseous reactant (NH₃) for which the two possible substitution products (ax or eq) would be energetically different.

Reactions of Os₃(CO)₁₁(NCCH₃) (1) and Os₃(CO)₁₁- (C_2H_4) (2) with Ammonia. It is known that 1 reacts in solution with NH₃ to form $Os_3(CO)_{11}(NH_3)^{16}$ (4). The same product is obtained when a CH_2Cl_2 solution of 2 is reacted with NH₃. (We have obtained slightly different IR and ¹H NMR data for 4 even when synthesizing 4 according to ref 16 (see Experimental Section).) Since its stereochemistry has not been assigned previously, we carried out a detailed NMR characterization

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Figure 2. Structure and ¹³C NMR spectrum (CD₂Cl₂, -70 °C) of a ¹³CO-enriched sample (\sim 40%) of Os₃(CO)₁₁(NH₃).

of 4. In solution 4 is fluxional and the ¹³C NMR spectrum (CD₂Cl₂) corresponding to its "frozen" structure is observed at -70 °C (Figure 2). It shows six resonances in the region for terminally bound CO ligands at $\delta = 189.8$ (2C, a/b), 185.2 (2C, b/a), 182.0 (1C, c), 179.4 (2C, d), 174.7 (2C, e/f), and 173.5 (2C, f/e). The number and relative intensities of the CO resonances clearly indicate that the ammonia ligand is bound in an axial position; for $M_3(CO)_{11}L$ complexes with L coordinated in an equatorial position eight CO resonances are expected. The signals at $\delta = 189.8$ and 185.2 show satellites due to ${}^{13}C - {}^{13}C$ J-coupling (36.6 Hz) characteristic of two carbonyl ligands in a trans arrangement¹⁷ and are therefore attributed to the axial carbonyls a and b. The remaining resonance in the axial CO region which has an intensity of 1 is assigned to the carbonyl trans to the ammonia ligand. The signals at $\delta = 179.4, 174.7$, and 173.5 correspond to the equatorial CO ligands labeled d, e, and f; their partial assignment follows from the dynamic behavior of $4.^{18}$ The structure of 4 derived from the low-temperature ¹³C limiting spectrum is analogous to that of the starting complex 1, and it is in agreement with the expectation that nitrogen donor ligands always occupy axial coordination sites in trimetallic carbonyl clusters.^{7,19,20}

When solid 1 or 2 are reacted with NH_3 at 80 °C for several hours (12–24 h), yellow powdery solids are obtained, the solution spectra (IR, ¹H, ¹³C) of which are identical to those of 4 (Scheme 2). The substitutions of the acetonitrile/ethene ligands in 1 and 2, respectively, by ammonia therefore occur in solution as well as in the solid state. The solid state reactions afford an analytical pure product (complete conversion into 4).

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Figure 3. ¹⁵N CPMAS spectrum (26 °C) of $Os_3(CO)_{11}$ (¹⁵-NH₃) (4a). Experimental conditions: spinning speed 6000 Hz, recycle time 12 s, contact time 3 ms, ambient temperature.



For the assignment of the stereochemistry of the solid state reactions the products had to be characterized in the solid state, since in solution 4 is fluxional and isomerization processes are likely to occur. Therefore, 1 and 2 were reacted at the solid state with $^{15}NH_3$ and

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the products were analyzed by ¹⁵N CPMAS spectroscopy. In both cases a sharp signal at $\delta = -467.0$ was observed (Figure 3) indicating that both 1 and 2 lead to the same stereoisomer of 4 (¹⁵NH₃ in an axial or equatorial coordination site should result in a different chemical shift). Furthermore the same ¹⁵N CPMAS spectrum is observed for Os₃(CO)₁₁(¹⁵NH₃) (4a) obtained by the solution reactions. Thus, also at the solid state only the ax-Os₃(CO)₁₁(NH₃) isomer is formed irrespective of the coordination site of the leaving group in the starting complexes.

For the observed site selectivity of the NH₃ ligand a fluxional behavior at some stage of the reactions has to occur as already found for the analogous reactions with CO. Also for the reactions with NH₃ a fluxional intermediate $Os_3(CO)_{11}$ would account for the observed stereochemistry (Scheme 3). Whereas the reaction of the $Os_3(CO)_{11}$ intermediate with ¹³CO leads to the two isoenergetical isomers (¹³CO in an axial or equatorial coordination site), the NH₃ ligand clearly favors the axial position (thermodynamically more stable).

No signal for a (hypothetical) equatorial isomer of $Os_3(CO)_{11}({}^{15}NH_3)$ is observed in the ${}^{15}N$ CPMAS spectrum even when the reaction is interrupted after short reaction times (e.g. 2 h, corresponding to ca. 40% conversion). There are two possible interpretations for this observation: (i) the $Os_3(CO)_{11}$ reacts with ammonia only when the vacant coordination site is in an axial position (kinetically controlled reaction), or (ii) both the ax and eq isomers are formed, but the less stable equatorial one reacts back or rearranges quickly to give the axial isomer (thermodynamically controlled reaction).

Since no other isomer is observed during the reaction, we cannot decide whether the formation of $ax-Os_3(CO)_{11}-(NH_3)$ is due to a site specificity of the NH_3 addition to $Os_3(CO)_{11}$ or to a rearrangement of the equatorially substituted isomer.

Reaction of Os₃(CO)₁₁(NCCH₃) (1) and Os₃(CO)₁₁-(C₂H₄) (2) with Dihydrogen. It has been shown by Poë et al.¹² that 1 reacts in solution with H₂ at 26 °C to form $(\mu$ -H)(H)Os₃(CO)₁₁ (5). When solid 1 and 2 are reacted with H₂ (1 atm) at 80 °C for 24 h a light yellow solid of Os₃(CO)₁₂ (3) and a violet sublimate of H₂Os₃-





 $(CO)_{10}$ (6) in an equimolar ratio are formed. The two products are nicely separated in the reaction apparatus and are obtained as pure compounds.

It can be assumed that the initial reaction with H_2 forms $(\mu$ -H)(H)Os₃(CO)₁₁ (5), which under the experimental conditions affords 3 and 6. In fact, when an authentic sample of 5 is heated to 80 °C, it completely converts into 3 and 6 within 24 h. Thus we propose that the solid state reactions of 1 and 2 proceed according to Scheme 4.

Conclusions

The results obtained in this work show that the "lightly stabilized" organometallic complexes 1 and 2, which are known to be very reactive in solution, also react readily in the solid state with gaseous reactants such as CO, NH_3 , and H_2 . The reactions apparently proceed via the coordinatively unsaturated species Os_3 -($CO)_{11}$, which is formed upon release of the acetonitrile/ ethene ligand (dissociative reaction pathway).

Since in the substitution reactions of the stereochemically different $Os_3(CO)_{11}L$ clusters 1 and 2 with ¹³CO and NH₃ the stereochemistry is lost (¹³CO) or selectively only one product stereoisomer is formed (NH₃), the unsaturated intermediate is proposed to be fluxional; in principle, both axial and equatorial coordination sites are therefore accessible for the incoming ligand.

In summary, these findings show that it is possible to generate coordinatively unsaturated, highly reactive organometallic species "in situ". Acetonitrile and ethene have been found to be good leaving groups; however, it may be interesting to explore systems containing bulkier groups as they are expected to be more labile. An alternative route to improve reaction rates may be provided by the control of the physical state of the solid substrate, such as its deposition in thin films on the walls of the reaction vessel or its physisorption on inert cellulosic supports.

In this account we dealt with simple addition reaction at the vacant site; however, one would expect that a number of chemical transformations could be carried out on the surface of metal clusters once suitable substrates have entered its coordination sphere.

Experimental Section

Materials. CO, NH₃, and H₂ were purchased from SIAD (Bergamo, Italy) and used without further purification. ¹³CO (99% enriched) and ¹⁵NH₃ (99% enriched) were purchased from Isotec (Miamisburg, OH). Os₃(CO)₁₁(NCCH₃),²¹ Os₃(CO)₁₁(C₂H₄),⁹ and H₂Os₃(CO)₁₁²² were prepared according to published methods. ¹³CO-enriched metal carbonyls were prepared by using as starting material ¹³C-enriched (ca. 40%) Os₃(CO)₁₂ obtained by direct exchange of ¹³CO with Os₃(CO)₁₂ (200 mg), in *n*-octane (100 mL) at 110 °C for 3 days in sealed vials (250 mL).

Spectra. Infrared spectra were recorded on a Perkin-Elmer 580B spectrometer. ¹H and ¹³C NMR spectra in solution were obtained on a JEOL EX400 spectrometer operating at 399.65 and 100.25 MHz, respectively. The high-resolution solid state ¹³C and ¹⁵N NMR experiments were performed on a JEOL GSE 270 (6.34 T) spectrometer operating at 67.8 and 27.4 MHz, respectively. Cylindrical 6 mm o.d. zirconia rotors with a sample volume of 120 μ L were employed with a spinning speed in the range from 5.5 to 6.0 kHz. For all samples the magic angle was carefully adjusted from the ⁷⁹Br MAS (magic angle spinning) spectrum of KBr by minimizing the line width of the spinning side bands from the satellite transitions.

The MAS technique was used for ${}^{13}C$, whereas in the case of ${}^{15}N$ the CPMAS technique was employed with a contact time

Reactions of Os₃(CO)₁₁(NCCH₃) (1) and Os₃(CO)₁₁-(C₂H₄) (2) with CO. A 50 mg amount of 1 (2) was introduced in a Schlenk tube apparatus (25 mL). The system was evacuated and refilled with CO (1 atm). The Schlenk apparatus was placed in an oil bath at 80 °C. After 24 h Os₃-(CO)₁₂ was formed quantitatively. The product was identified by IR (KBr pellets).²³

Reactions of Os₃(**CO**)₁₁(**NCCH**₃) (1) and **Os**₃(**CO**)₁₁(**C**₂**H**₄) (2) with NH₃. A 50 mg amount of 1 (2) was exposed to NH₃ gas (1 atm) at 80 °C in a Schlenk tube apparatus (25 mL). After 24 h yellow Os₃(CO)₁₁(NH₃) (4) was formed quantitatively. The product was identified by IR and NMR. IR: ν (CO) (cm⁻¹) (CH₂Cl₂) 2104 (w), 2050 (s), 2034 (vs), 2019 (m), 1996 (s), 1985 (sh), 1960 (sh); ν (NH₃) (cm⁻¹) (KBr) 3390, 3316; δ (NH₃) (cm⁻¹) 1626, 1290, 1277. ¹H NMR (acetone-*d*₆, 25 °C): δ = 4.09 (broad). ¹³C NMR (CD₂Cl₂, -70 °C): δ = 189.8 (2), 185.2 (2), 182.0 (1), 179.4 (2), 174.7 (2), 173.5 (2).

Reactions of Os(CO)₁₁(NCCH₃) (1) and Os₃(CO)₁₁(C₂H₄) (2) with H₂. A 50 mg amount of solid 1 was exposed to H₂ (1 atm) at 80 °C. After 24 h the starting material was completely converted into a violet sublimate $(H_2Os_3(CO)_{10})$ and a light yellow solid $(Os_3(CO)_{12})$ in an equimolar ratio. The products were identified by IR (KBr pellets).^{23,24}

 $Os_3(CO)_{11}(^{13}CO)$ (3a) and $Os_3(CO)_{11}(^{15}NH_3)$ (4a) were obtained as described above using ^{13}CO and $^{15}NH_3$, respectively. The reaction times for the solid state reactions indicate only the order of magnitude as they depend upon the particle size of the solid substrate.

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