Reactions of Solid $H_2Os_3(CO)_{10}$ with Gaseous CO, NH_3, and H_2S

Silvio Aime,* Walter Dastrù, and Roberto Gobetto

Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali, Università di Torino, via Pietro Giuria 7, 10125 Torino, Italy

Alejandro J. Arce

Chemistry Center, Instituto Venezolano de Investigationes Cientificas, Apartado 21827, Caracas 1020-A, Venezuela

Received February 28, 1994®

The coordinatively unsaturated $H_2Os_3(CO)_{10}$ (**1**) cluster reacts readily in the solid state with gaseous reactants L (L = CO, NH_3, H_2S) to afford the electron-precise adducts $H_2Os_3(CO)_{10}L$ (**2**, L = CO; **3**, L = NH_3; **4**, L = H_2S). In the case of the reaction with CO, the solid product **2** was unambiguously characterized by means of ^1H magic angle spinning NMR spectroscopy. Upon longer reaction times compound **2** releases H_2 and transforms into $Os_3(CO)_{12}$ (**5**). The novel NH_3 adduct **3** exists in solution as a mixture of two isomers, differing in the relative orientation of the ammonia and the terminal hydride ligands with respect to the Os_3 plane (syn and anti). Variable-temperature (VT) ^1H and ^{13}C NMR spectroscopy revealed that these isomers interconvert in solution. The novel H_2S adduct **4** was much less stable than the other two, and upon dissolution in dichloromethane, it immediately transformed into the known compound $H_2Os_3(CO)_9S$ (**6**).

Introduction

In recent years, solid–gas reactions have been under intense scrutiny[1–5] for several reasons. A general interest in developing solid-state reactions lies in the possibility of avoiding the use of solvents with the obvious positive environmental implications. Next, there is the expectation that the topochemical control occurring in these reactions may result in the formation of products different from those obtained from the same reactions in solution. Furthermore, it is likely that solid-state reactions may give rise to single products, whereas in solution the same reactions may produce a number of products. In fortunate cases it may be possible to "freeze out" transition states,[6] whose structures may then be characterized by spectroscopic techniques. The assessment of the structural features of the activated states is of paramount importance in the elucidation of reaction pathways.

How can a reaction between a solid substrate and a gaseous reactant proceed? In principle, one may envisage two possible pathways. (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, thus disrupting the crystalline order and allowing further substrate molecules to interact with the gaseous reactant which penetrates the interlayer spaces; to get a bulk reactivity, such a process may require the sliding of the product species over the surface of the solid.

Thus, such a solid-state reaction can only proceed if two requirements are met: (i) the surface reaction is spontaneous, and (ii) the reaction product separates from the solid substrate. Alternatively, the transformation of the uppermost layer can cause an "expansion" of the lattice, thus allowing the gaseous reactant to disperse into it.

We accomplish requirement i by using the cluster compound $H_2Os_3(CO)_{10}$ (**1**), which is coordinatively unsaturated and which is known[7–13] to react instantaneously in solution with a number of Lewis bases L to afford the $H_2Os_3(CO)_{10}L$ adducts as a result of ligand addition to the metal cluster:

$$H_2Os_3(CO)_{10} + L \leftrightarrow H_2Os_3(CO)_{10}L$$

$$L = CO, PR_3, CNR, Cl^-, Br^-, ...$$

An additional advantage of studying the solid-state reactivity of **1** is that the loss of the cluster unsaturation is invariably manifested by the disappearance of its intense violet color.

Results and Discussion

Reaction of Solid 1 with CO. As a first attempt to test the practicality of a solid–gas reaction, we inves-

---

® Abstract published in *Advance ACS Abstracts,* October 1, 1994.

[1] Thomas, J. M.; Moro, S. E.; Desvergne, J. P. *Adv. Phys. Org. Chem.* **1977,** *15,* 63.

[2] Chin, C. S.; Lee, B.; Kim, S. *Organometallics* **1993,** *12,* 1462.

[3] Bianchini, C.; Peruzzini, M.; Zanobini, F. *Organometallics* **1991,** *10,* 3415.

[4] Bianchini, C.; Farnetti, E.; Graziani, M.; Kaspar, J.; Vizza, F. *J. Am. Chem. Soc.* **1993,** *115,* 1753.

[5] Siedle, A. R.; Newmark, R. A. *J. Am. Chem. Soc.* **1989,** *111,* 2058.

[6] Bianchini, C.; Zanobini, F.; Aime, S.; Gobetto, R.; Psaro, R.; Sordelli, L. *Organometallics* **1993,** *12,* 4757.

[7] Deeming, A. J.; Hasso, S. *J. Organomet. Chem.* **1975,** *88,* C21.

[8] Deeming, A. J.; Hasso, S. *J. Organomet. Chem.* **1976,** *114,* 313.

[9] Keister, J. B.; Shapley, J. R. *Inorg. Chem.* **1982,** *21,* 3304.

[10] Shapley, J. R.; Keister, J. B.; Churchill, M. R.; De Boer, B. G. *J. Am. Chem. Soc.* **1975,** *97,* 4145.

[11] Churchill, M. R.; De Boer, B. G. *Inorg. Chem.* **1977,** *16,* 2397.

[12] Churchill, M. R.; De Boer, B. G. *Inorg. Chem.* **1977,** *16,* 878.

[13] Adams, R. D.; Golembeski, N. M. *Inorg. Chem.* **1979,** *18,* 1909.

0276-7333/94/2313-4232$04.50/0

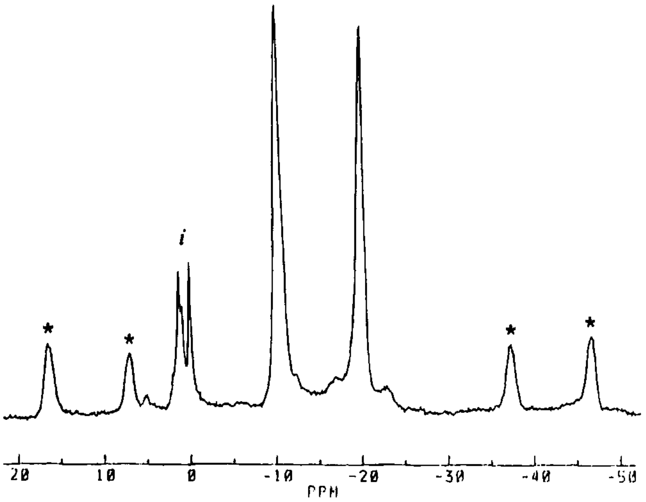


Figure 1. ^1H MAS NMR spectrum at 300 MHz of $H_2Os_3(CO)_{11}$ (**2**) in the solid state (32 transients, recycle delay 60 s, spinning speed 8 kHz). The asterisks denote the spinning sidebands flanking the isotropic peaks; i indicates residual solvent impurities.

tigated the interaction between solid **1** and CO. A reaction takes place at a reasonable rate only at temperatures significantly higher than ambient temperature. For instance, 50 mg of **1** fully reacted in the presence of 1 atm of CO at 80 °C after 12 h. The transformation of **1** affords a yellow material, the ^1H NMR spectrum of which (CD_2Cl_2 solution) showed at -60 °C the characteristic high-field absorptions of the bridging (-20.02 ppm, $^2J_{H,H} = 3.8$ Hz) and terminal (-10.30 ppm, $^2J_{H,H} = 3.8$ Hz) hydrides reported for $H_2Os_3(CO)_{11}$ (**2**).[7,9]

In order to establish that **2** was not produced during the dissolution in CD_2Cl_2, we recorded a high-resolution ^1H MAS NMR spectrum of the yellow product. By rotating the sample at high speeds (>8 kHz), we observed two relatively sharp signals at -20.1 and -10.5 ppm (Figure 1). This evidence convinced us that **2** had already formed in the solid–gas reaction. Further support arises from the similarity of the solid-state IR spectrum of the reaction product (Figure 2a) with that reported[7] for **2** in hydrocarbon solution. Thus, under these experimental conditions, the solid–gas reaction proceeds to the complete conversion of **1** into **2**.

Upon prolonged heating, this reaction affords variable amounts of $Os_3(CO)_{12}$ (**5**); i.e. compound **2** releases H_2 and transforms into **5**. This latter transformation appears favored by the fact that **2** is produced, in this solid–gas reaction, under the form of an highly dispersed material. In fact, a negligible formation of **5** is detected when a crystalline sample of **2** is reacted, under the same experimental conditions, with CO. On the other hand, the observation that the solid–gas reaction proceeds more readily when the organometallic material is finely dispersed appears quite general. For instance, we found that the reaction of **1** with CO occurs much more promptly when the starting material is placed as a thin film on the wall of the reaction vessel. The formation of **5** from the further reaction of **2** with CO implies the evolution of a molecule of H_2 for each molecule of product. This behavior parallels what is observed in solution.[14] Although from these experiments we have not obtained any insight into the operating mechanism, the observed transformation suggests that, also under the relatively mild experimental conditions used in this work, there is the possibility for extensive intramolecular rearrangement such as that required for the H_2 elimination process.

Reaction of Solid 1 with NH_3. The success obtained in the production of solid $H_2Os_3(CO)_{11}$ (**2**) prompted us to react **1** with NH_3 in order to prepare the adduct $H_2Os_3(CO)_{10}(NH_3)$ (**3**), which has not yet been reported from solution studies. This reaction proceeds quickly, and we observe the complete disappearance of the violet color already after 2 h at room temperature in presence of 1 atm of NH_3 gas. The yellow product shows an IR spectrum (KBr pellet) in the CO region (Figure 2b) quite similar to that found for solid $H_2Os_3(CO)_{11}$ (**2**). In addition, it shows two weak absorptions at 3377 and 3361 cm^{-1} (stretching modes of NH_3[15]) and three medium-intensity absorptions at 1620, 1285, and 823 cm^{-1} (bending modes of coordinated NH_3) which definitely suggest the formation of the adduct **3**. Solid **3** is stable for prolonged periods only in the presence of NH_3 and decomposes immediately when dissolved in chlorinated solvents, yielding **1** and free NH_3. However, the compound appears to be stable enough in toluene solution to allow full characterization by NMR spectroscopy.

^1H and ^{13}C NMR Spectra of 3. The ^1H NMR spectrum (Figure 3) of **3** at -60 °C in toluene solution shows three main resonances in the relative intensity ratio of 3:1:1 at 0.19 ppm (NH_3 protons), -10.53 ppm (terminal hydride), and -16.44 ppm (bridging hydride), respectively. The observed coupling of the two hydrides ($^2J_{H,H} = 4.0$ Hz) is in agreement with the corresponding values reported for other $H_2Os_3(CO)_{10}L$ adducts.[9] The signal at 0.19 ppm has been unambiguously assigned to the coordinated NH_3 ligand on the basis of the spectrum of the isotopomer containing $^{15}NH_3$ (**3a**). The NH_3 protons of **3a** give rise to a doublet due to the coupling with the ^{15}N nucleus. The observed coupling constant $^1J_{^{15}N,H} = 70.5$ Hz is slightly larger than the value of 61.2 Hz reported[16,17] for NH_3 gas. In effect, an increase in the value of the $^1J_{^{15}N,H}$ coupling constant is expected when the nitrogen is coordinated to a metal center.[18]

The ^{13}C NMR spectrum of a toluene solution of ^{13}C-enriched **3** recorded at 233 K shows 10 CO resonances of equal intensity (Figure 4) at 188.3, 184.8, 181.1, 176.6, 176.5, 175.4, 175.1, 173.9, 173.4, and 173.3 ppm, respectively. A partial assignment of the carbonyl resonances was straightforward on the basis of the following coupling features. (i) A $^2J_{C,C}$ value of 35.1 Hz is observed between resonances at 188.3 and 184.8 ppm; since this coupling pattern is typical for a trans carbonyl arrangement, we assign these resonances to CO_g and CO_i (Chart 1). (ii) A $^2J_{C,H}$ coupling of 21.4 Hz is observed for the resonance at 181.1 ppm, which is therefore assigned to CO_a trans to the terminal hydride; the carbonyls at 173.9 and 173.3 ppm show a smaller

---

[14] Poë, A. J.; Sampson, C. N.; Smith, R. T.; Zheng, Y. *J. Am. Chem. Soc.* **1993**, *115*, 3174.

[15] Nakamoto, Z. K. *Infrared Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1970; pp 150–160.

[16] Litchman, W. M.; Alei, M.; Florin, A. E. *J. Chem. Phys.* **1969**, *50*, 1031.

[17] Litchman, W. M.; Alei, M.; Florin, A. E.; O'Brien, J. F. *J. Phys. Chem.* **1971**, *75*, 932.

[18] Mason, J. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987; pp 357–362.

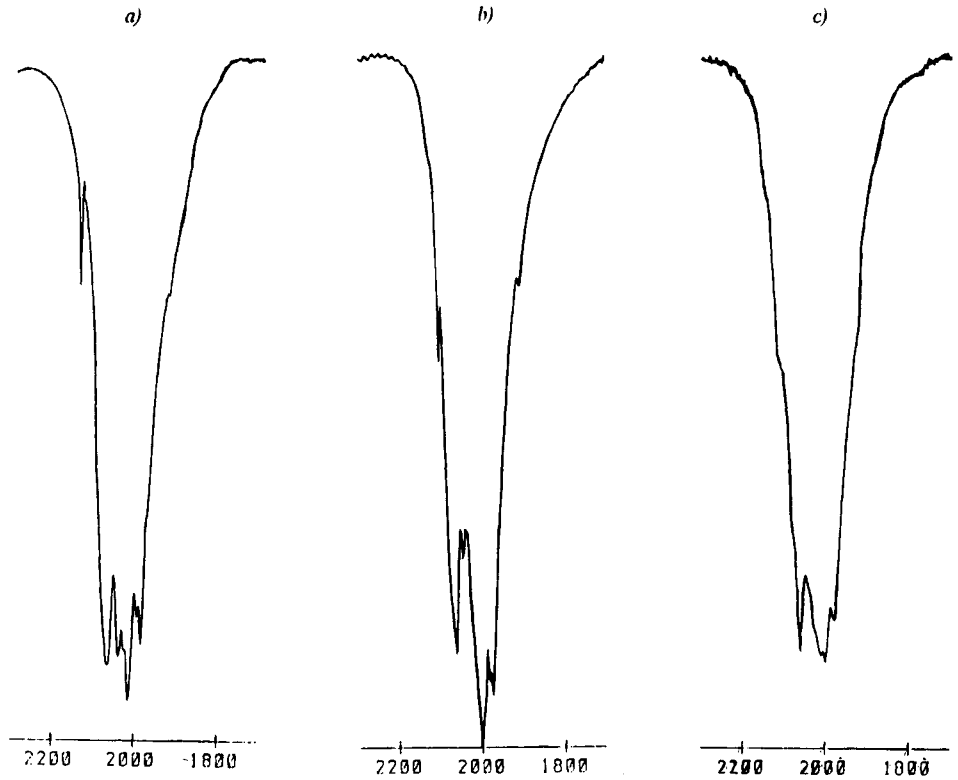
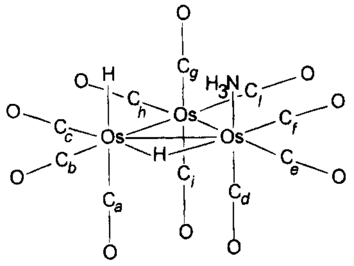


Figure 2. IR spectra (KBr pellet) in the carbonyl region of (a) $H_2Os(CO)_{11}$ (**2**) (b) $H_2Os_3(CO)_{10}(NH_3)$ (**3**), and (c) $H_2Os_3(CO)_{10}(H_2S)$ (**4**).

Chart 1



C—H coupling ($^2J_{C,H}$ = 13.0 Hz and $^2J_{C,H}$ = 11.2 Hz, respectively) with the bridging hydride and are therefore assigned to carbonyls c and f.

A more complete inspection in the low-temperature limiting ^1H spectrum (Figure 3, 213 K) of the hydride region revealed another set of very low intensity resonances at −9.16 ppm (terminal hydride) and −17.04 ppm (bridging hydride) assigned to a second isomer of **3**. The signal for the NH_3 protons of this minor isomer is overlapped by the signal of the corresponding protons of the major isomer. The two isomers are easily accounted for by the two possible relative orientations of the terminal hydride and the NH_3 ligand (syn and anti with respect to the Os_3 plane). An NOE (nuclear Overhauser effect) measurement through the saturation of ammonia protons showed that in the major isomer the NH_3 ligand and the terminal hydride are on the same side of the Os_3 plane.

Syn/Anti Isomerization of 3. When the temperature is increased from 213 to 296 K (Figure 3), the hydride resonances of the major isomer broaden and then sharpen again at 313 K. Since this process is accompanied by the disappearance of the hydride resonances of the minor isomer, we conclude that the dynamic process occurring (Scheme 1) is an isomerization which involves the exchange of the terminal hydride of the major species with the bridging hydride of the minor one, and vice versa. A slight change of the chemical shifts toward the position of the exchanging partner of the minor species is clearly detectable as one goes from the low- to the high-temperature limiting spectrum.

The VT^{13}C NMR spectra fully support the exchange mechanism postulated on the basis of the VT ^1H NMR spectra. In fact, as the temperature is increased (Figure 4), we observe only a broadening and minor shifts of most of the resonances (more severe for CO_a and CO_c) followed by their sharpening up. This behavior can be interpreted in terms of an exchange between the resonances of a large-majority isomer with the very low (not detectable) resonances of the minor isomer. Of course, CO_a and CO_c are the most affected, because in the proposed exchange pattern they exchange with $CO_{c'}$ and $CO_{a'}$, respectively, of the minor isomer, thus involving a relatively large chemical shift separation between the exchanging resonances.

In the presence of an excess of NH_3, separate and sharp ^1H NMR resonances for free (−0.17 ppm at 213 K in toluene) and coordinated ammonia are observed over the whole temperature range, thus excluding an exchange of free and coordinated ammonia. It follows that also the syn/anti isomerization observed for **3** must be an intramolecular process.

Reaction of 1 with H_2S. When solid **1** is treated with H_2S (1 atm) at room temperature, the violet color of the starting material disappears and a yellow solid is formed. A complete conversion is already observed after few minutes. The IR pattern (KBr pellet) of the product (Figure 2c) is very similar to that observed for $H_2Os_3(CO)_{11}$ (**2**) and $H_2Os_3(CO)_{10}(NH_3)$ (**3**) and therefore strongly supports the formation of the analogous adduct

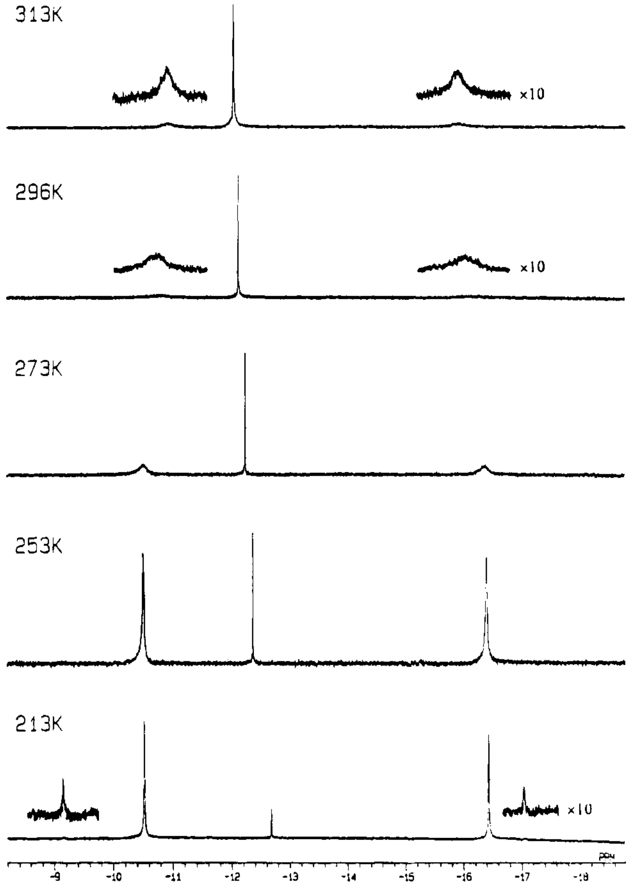


Figure 3. VT ^1H NMR spectra of $H_2Os_3(CO)_{10}(NH_3)$ (**3**) at 399.65 MHz (solvent toluene-d_8). The signal at −12.68 ppm at −60 °C corresponds to $H_2Os_3(CO)_{10}$ (**2**).[23] Its intensity grows as the temperature increases as a consequence of partial decomposition of $H_2Os_3(CO)_{10}(NH_3)$ (**3**).

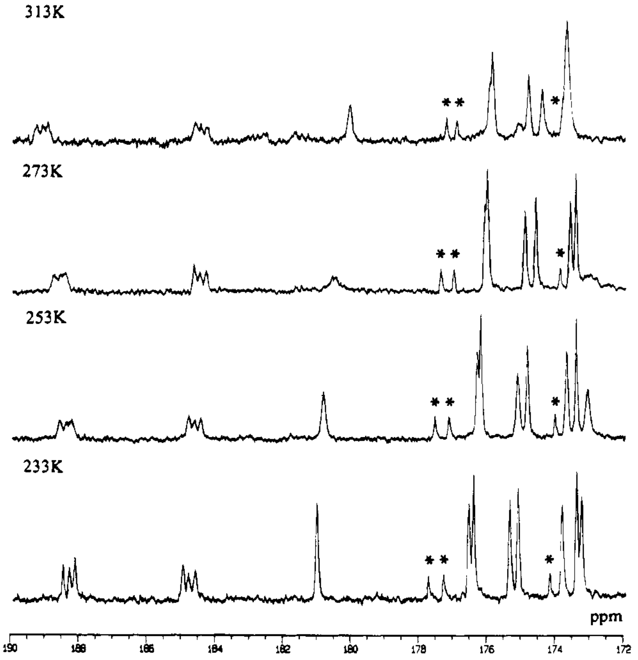
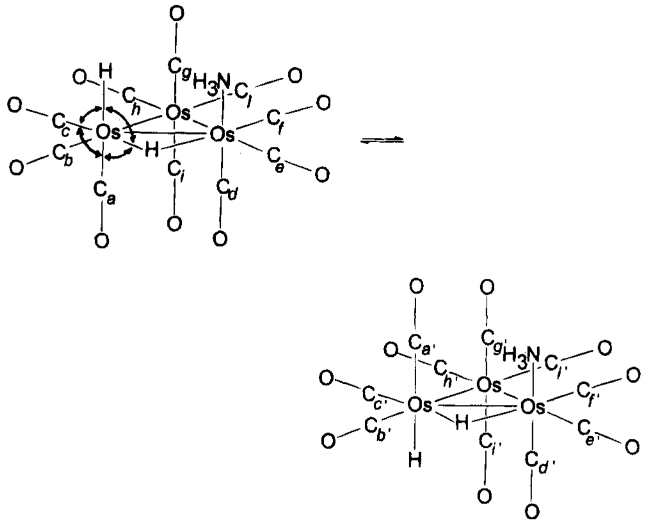


Figure 4. VT ^{13}C NMR spectra of $H_2Os_3(CO)_{10}(NH_3)$ (**3**) at 100.25 MHz (solvent toluene-d_8). The low-intensity resonances (labeled with asterisks) correspond to a not yet characterized product arising from prolonged standing of a solution of **3** in a sealed vial at room temperature.

Scheme 1



$H_2Os_3(CO)_{10}(H_2S)$ (**4**). However, dissolution of this product in CD_2Cl_2, hexane, or toluene leads to a yellow solution whose spectroscopic characterization (^1H and ^{13}C NMR, IR) unambiguously indicates the presence of $H_2Os_3(CO)_9S$ (**6**).[19,20] Thus, it appears that the adduct **4** is stable only in the solid state, whereas in solution it readily converts into **6** with cleavage of the S—H bond and concomitant loss of CO and H_2.

Conclusions

In summary, the results herein reported show that solid−gas reactions can be readily carried out by using the coordinatively unsaturated $H_2Os_3(CO)_{10}$ (**1**) cluster. In all three reactions investigated, the transformation is complete and invariably a single product is obtained. The different experimental conditions (time and temperature) necessary to achieve the complete conversion of **1** into **2**, **3**, and **4**, respectively, may be accounted for by different abilities of the products to separate from the bulk crystal of unreacted **1**.

Our experiments do not provide any information on the intimate mechanism of the addition of gaseous CO, NH_3, and H_2S, respectively, to solid **1**. However, some insight may be obtained on the basis of the results of a detailed study on the reaction kinetics and thermodynamics of the $H_2Os_3(CO)_{10}$−CO system carried out by Poë and co-workers.[14] The observation that the reactions with NH_3 and H_2S readily occur at the solid/gas interface even at room temperature appears to rule out the occurrence of a mechanism in which the formation of the $H_2Os_3(CO)_{10}L$ adduct involves an initial, highly reversible, bridge-to-terminal movement of one bridging hydride ligand in **1**. In fact, it has been reported that the zero-field ^1H NMR[21] in the solid state of **1** does not show any evidence of mobility inside the hydride moiety at room temperature. Tentatively, we consider as a likely pathway for the solid/gas reaction a mechanism in which the ligand addition step to the doubly bridged cluster precedes or occurs simultaneously with the bridge to terminal movement of one hydride ligand. On the other hand, the mobility of the hydride ligands

---

(19) Forster, A.; Johnson, B. F. G.; Lewis, J.; Matheson, T. W. *J. Organomet. Chem.* **1976**, *104*, 225.

(20) Braker-Novak, J.; Hajela, S.; Lord, M.; Zhang, M.; Rosemberg, E.; Gobetto, R.; Milone, L.; Osella, D. *Organometallics* **1990**, *9*, 1379.

(21) Zax, D. B.; Bielecki, A.; Kulzick, M. A.; Muetterties, E. L.; Pines, A. *J. Phys. Chem.* **1986**, *90*, 1065.

appears likely in $H_2Os_3(CO)_{11}$ (**2**) because this process is expected to anticipate the dissociative loss of H_2.

These observations suggest that the extremely rich chemistry shown by $H_2Os_3(CO)_{10}$ in solution can be further widened by exploring its reactivity in the solid state. Furthermore, it will be worthwhile to assess if organometallic compounds containing good leaving groups can afford coordinatively unsaturated species in the solid state whose reactivity might then be fully exploited.

Experimental Section

Materials. CO, NH_3, and H_2S gases were purchased from SIAD (Bergamo, Italy) and used without further purification. ^{13}CO (99% enriched) was purchased from Isotec (Miamisburg, OH). $^{15}NH_3$ (99% enriched) was purchased from Euriso-Top (Saint-Aubin, France). $H_2Os_3(CO)_{10}$ (**1**) was prepared according to the published method.[22] The ^{13}CO-enriched sample of **1** was prepared from a ^{13}CO-labeled sample of $Os_3(CO)_{12}$ (**5**), obtained by direct exchange of ^{13}CO with **5** in *n*-octane at 110 °C for 3 days in sealed vials (250 mL). The level of enrichment was ~55%, as judged from the isotopomer populations.

Spectra. ^1H and ^{13}C NMR spectra in solution were obtained on a JEOL EX400 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 580B spectrometer. The ^1H MAS NMR spectrum of **2** was recorded on a Bruker MSL 300 spectrometer operating at 300 MHz (University College, London, U.K.).

Reaction of 1 with CO. **1** (50 mg) was introduced into a Schlenk-tube apparatus. The system was evacuated and refilled with CO (1 atm). The Schlenk apparatus was placed in a oil bath at 353 K for 12 h, during which time the color changed from violet to pale yellow. After removal of the gas, the solid product was kept under nitrogen. Identification of the product was made in the solid state and in solution by IR (KBr pellet and cyclohexane, respectively), ^1H NMR (MAS and CD_2Cl_2 solutions), and ^{13}C NMR (CD_2Cl_2 solutions). IR (KBr pellet): 2137 (m), 2064 (s), 2036 (s), 2022 (sh), 2013 (vs), 1992 (m), 1983 (m), 1923 (vw, sh) cm^{-1}.

Reactions of 1 with NH_3. **1** (50 mg) was exposed to NH_3 gas (1 atm) at 298 K in a Schlenk-tube apparatus. After 2 h the color completely changed from violet to pale yellow. Identification of the product was made in the solid state and in solution by IR (KBr pellet) and ^1H NMR and ^{13}C NMR (toluene-d_8 solutions). IR (KBr pellet): 3377 (w), 3361 (w), 2100 (m), 2062 (s), 2042 (m), 2000 (vs), 1981 (m), 1973 (m), 1900 (vw, sh), 1620 (w), 1285 (m), 823 (w) cm^{-1}.

Reaction of 1 with H_2S. **1** (50 mg) was allowed to react with H_2S gas (1 atm) at 298 K for 2 h. After removal of the gas, the solid product was kept under nitrogen. Identification of the solid product was made by IR spectroscopy (KBr pellet): 2117 (sh), 2059 (s), 2009 (s), 1997 (s), 1982 (m), 1977 (m) cm^{-1}. When the solid material was dissolved in CH_2Cl_2, it instantaneously afforded $H_2Os_3(CO)_9S$ (**6**), characterized by ^1H NMR, ^{13}C NMR, and IR spectroscopy.[19,20]

Acknowledgments. We thank Dr. P. J. Barrie, University College, London, U.K., for recording the ^1H MAS NMR spectrum of $H_2Os_3(CO)_{11}$. We thank the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST, Rome) for financial support.

OM940153T

---

(22) Kaesz, H. D. In *Inorganic Syntheses*; Angelici, R. J., Ed.; Wiley: New York, 1990; Vol. 28, pp 238–239.

(23) Note that the ^1H chemical shift of $H_2Os_3(CO)_{10}$ is strongly solvent dependent since it goes, at 213 K, from −11.50 ppm in CH_2Cl_2 to −12.68 ppm in toluene.