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Addition of NH_3 to the Cluster Complexes $M_3H(\mu\text{-}H)(CO)_{11}$ (M = Ru, Os)

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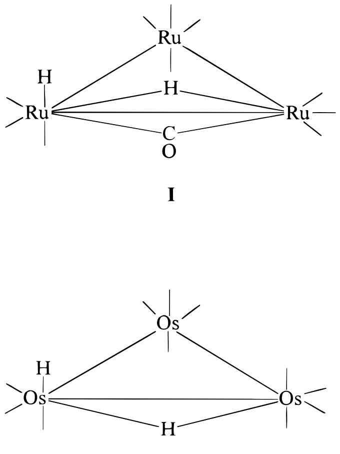
The reactions of ammonia with either $Ru_3H(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}$ (**I**) or $Os_3H(\mu\text{-}H)(CO)_{11}$ (**II**) in CD_2Cl_2 solutions yield $[NH_4]^+[M_3(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}]^-$ (M = Ru, Os). When the reactions are followed at low temperature (183 K) by means of ^1H, ^{13}C, and ^{15}N NMR spectroscopy, it is possible to detect the formation of kinetic products which are derived from the addition of an ammonia molecule to a carbonyl carbon atom. In the Ru case ammonia is bonded to the bridging carbonyl carbon atom and maintains its wholeness. In the Os system a carbamoyl moiety is formed by transfer of one hydrogen from NH_3 to the oxygen atom of the carbonyl group to form an O−H bond. The NMR observation of the latter functionality is prevented by the occurrence of a fast proton exchange with the excess of free NH_3 present. Two isomers of this carbamoyl-containing species can be detected; the structural difference between them is based only on which carbonyl has undergone the ammonia attack.

Introduction

Studies on the reactivity of ammonia and related amines have received limited attention in cluster chemistry. Only in the cases of the reactions with the coordinatively unsaturated $Os_3(\mu\text{-}H)_2(CO)_{10}$ cluster[1a] and $Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_6N)$,[1b] with the lightly stabilized $Os_3(CO)_{11}(NCCH_3)$,[1c,d] and with the reactive saturated cluster $Os_3(\mu\text{-}H)(CO)_9(C{=}N(CH_2)_3)$[2] has direct coordination of ammonia to the metallic center been found. In the last case a solid-state structure of the complex has been reported. In other cases the amines give either nucleophilic attack or oxidative addition reactions. Kaesz and co-workers investigated the reaction of dimethylamine with $Ru_3(CO)_{12}$ and found that it produces the $Ru_3(\mu\text{-}H)[\mu\text{-}\eta^2\text{-}OCN(CH_3)_2](CO)_{10}$ cluster compound.[3] Whereas the latter reaction occurs under very mild conditions (it starts at 243 K), the analogous reaction with aniline occurs in refluxing benzene and yields the amido-bridged complex $Ru_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}NHPh)(CO)_{10}$.[4] Finally, several examples of nucleophilic attack of ammonia and other amines to alkynyl, allenyl, and allyl ligands coordinated to the cluster frameworks have been reported.[5]

We decided to investigate the reactivity of NH_3 and related amines with $Ru_3H(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}$ (**I**) and $Os_3H(\mu\text{-}H)(CO)_{11}$ (**II**) (Chart 1)[6−8] in order to assess which of the possible reactions (H_2 or CO substitution, nucleophilic attack at a carbonyl carbon atom, or acid−base reaction) takes place in these systems. Furthermore, since **I** displays a bridging carbonyl ligand whereas **II** possesses all terminal carbonyl groups, we were interested in determining if such a structural difference had any effect on the reactivity of the complexes. The reactions were followed up also at low temperature in order to get more insight into the understanding of the initial reaction steps.

Chart 1



I

II

Results and Discussion

When NH_3 gas is flowed into CD_2Cl_2 solutions containing **I** or **II** at room temperature, a net transformation into $[NH_4]^+[M_3(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}]^-$ (M = Ru, Os) occurs (Scheme 1). Their characterization was carried

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[1] (a) Aime, S.; Dastrù, W.; Gobetto, R.; Arce, A. J. *Organometallics* **1994**, *13*, 4232. (b) Bar Din, A.; Bergman, B.; Rosenberg, E.; Smith, R.; Dastrù, W.; Gobetto, R.; Milone, L.; Viale, A., *Polyhedron*, in press. (c) Süss-Fink, G. *Z. Naturforsch*. **1980**, *35B*, 454. (d) Aime, S.; Dastrù, W.; Gobetto, R.; Krause, J.; Sappa, E. *Organometallics* **1995**, *14*, 3224.

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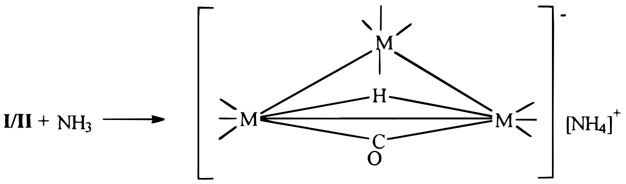
Scheme 1



out on the basis of the comparison of their elemental analysis and IR and ^{13}C and ^1H NMR spectra with literature data.[10] Minor differences have been observed for the chemical shifts of the bridging ^{13}C-carbonyl and ^1H-hydride resonances, as a consequence of the different counterions.

One may conclude that the observed behavior simply consists of extraction by the base NH_3 of one proton from the dihydride metal carbonyl derivatives to yield the monohydride carbonyl anions.

To get more insight into the reaction pathways which lead to the formation of the $[NH_4]^+[M_3(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}]^-$ (M = Ru, Os) species, we investigated these reactions directly in the NMR tube at 183 K. Also at this temperature the reactions eventually yield $[NH_4]^+[M_3(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}]^-$, but there is clear evidence for the formation of kinetic products in both reactions. These derivatives are sufficiently stable at low temperature to allow their full characterization by ^1H, ^{13}C, and ^{15}N NMR spectroscopy. Although the two final products are isostructural,[9] there are noticeable structural differences between the kinetic species found in the two reactions.

Low-Temperature Reaction of I with NH_3 and Related Amines. The intermediate (**IA**) from the reaction between **I** and NH_3 (100 Torr) at 183 K is characterized by three absorptions in the ^1H NMR spectrum (CD_2Cl_2, 183 K) at 2.18 (3H, broad), −11.7 (1H, $^2J_{^1H,^1H} = 2.0$ Hz), and −16.1 ppm (1H, broad, half-height width 5.5 Hz), respectively. The broadening of the coordinated NH_3 resonance at 2.18 ppm and of the hydride signal at −16.1 ppm does not appear to be associated with unresolved $J_{^1H,^1H}$ couplings between them, since it cannot be reduced by selectively decoupling one signal while observing the other one. On the other hand, irradiation of the hydride signal at −16.1 ppm causes the merging of the doublet at −11.7 ppm into a sharp singlet. When the hydride NMR regions of **I** and **IA** are compared, it is evident that the interaction with NH_3 produces a larger variation in the bridging hydride chemical shift with respect to the terminal one. Furthermore, the spin−lattice relaxation time T_1 of the former is slightly shorter than that of the latter (2.09 s for the bridging hydride and 2.76 s for the terminal hydride at 183 K) and suggests a closer interaction of the ammonia protons with the bridging hydride.

The ^{13}C NMR spectrum of **IA** (CD_2Cl_2, 183 K, Figure 1) shows 10 terminal carbonyl resonances at 203.7, 202.4, 199.1 ($^2J_{^{13}C,^1H_{term}} = 13.6$ Hz), 198.8 ($^2J_{^{13}C,^1H_{term}} = 13.6$ Hz), 196.4, 195.4, 194.0 ($^2J_{^{13}C,^1H_{bridge}} = 13.2$ Hz), 188.1, 186.6, and 185.6 ppm, respectively, and a broad signal at 279.9 ppm (half-height width 25.7 Hz) typical of a bridging carbonyl. The overall patterns of hydride and carbonyl NMR regions are similar to the corresponding spectra of the parent complex **I**. This suggests that **IA** is the product resulting from the simple addition of NH_3 to **I**; i.e., the molecular formula $Ru_3H(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}(NH_3)$ can be assigned to **IA**.

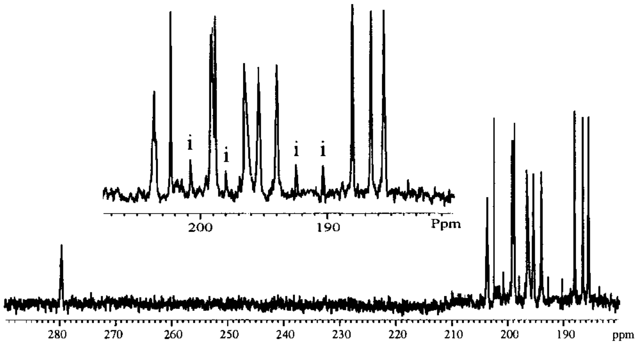
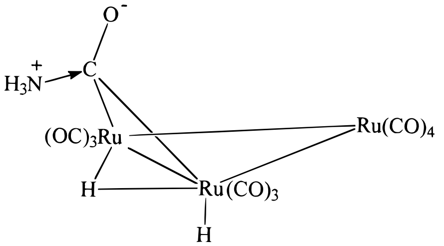


Figure 1. $^{13}C\{^1H\}$ NMR spectrum of **IA** (CD_2Cl_2, 183 K; i denotes impurities.

Chart 2



By using $^{15}NH_3$ as reagent, it is possible to detect the ^{15}N NMR absorption (CD_2Cl_2, 183 K) of bound NH_3 at −421.6 ppm (quartet, $^1J_{^{15}N,^1H} = 70.0$ Hz), which is about 45 ppm upfield than that of free ammonia.

In a ^{13}C, ^{15}N doubly enriched sample a $^1J_{^{15}N,^{13}C}$ value of 10.0 Hz can be observed in the ^{15}N NMR spectrum, whereas no $^1J_{^{15}N,^{13}C}$ is detected in the ^{13}C NMR spectrum. This odd result suggests that the $^{15}N-^{13}C$ coupling deals with the broad bridging CO resonance. In fact, if the coupling involved any other CO group, it would also be detected in the ^{13}C NMR spectrum, since all the terminal CO resonance line widths are <5 Hz.

On the basis of these spectroscopic data, we suggest that in the $Ru_3H(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}(NH_3)$ adduct the ammonia nitrogen is bound to the bridging carbonyl carbon atom (Chart 2). The close similarity in the ^{13}C chemical shifts and $^2J_{^{13}C,^1H}$ values in **I** and **IA** is consistent with the maintainance of the basic structural features of **I** upon formation of the adduct.

The cause of the broadening of the bridging CO resonance is not clear. There may be a contribution from unresolved $^2J_{^{13}C,^{13}C}$ couplings, but this seems to be a minor effect, since it would have been detected in some of the terminal carbonyl resonances as well. Another possibility is the effect of the quadrupolar ^{14}N nucleus. However, this explanation has to be ruled out since no significant change in the bridging CO resonance line width is detected in the ^{15}N-containing isotopomer.

Tentatively, we may relate the peculiar broadening of the bridging CO and hydride ligands to the asym-

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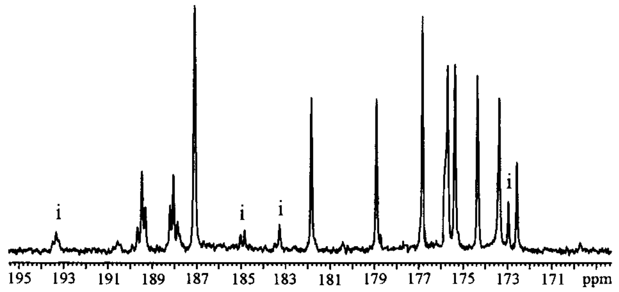


Figure 2. $^{13}C\{^1H\}$ NMR spectrum of **IIA** (CD_2Cl_2, 183 K; i denotes impurities.

metric environment on the two sides of the bridging moieties. One may envisage that the process of sticking the ammonia molecule to $Ru_3H(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}$ affords several structures having similar energy: this would give rise to a dispersion of chemical shifts, i.e. to the observed broadening of the bridging ligand signals.

Since a higher acidic character has been associated with the bridging hydrides rather than with the terminal ones,[10] it seems reasonable to suggest that the proton abstraction to form the NH_4^+ cation involves the bridging hydride ligand, whose coordination site is then replaced by the transformation of the terminal hydride into a bridging one.

To establish the effect of the ligand basicity on the reaction, we carried out the reactions of **I** with some substituted amines and we found that the ease of formation of $[LH]^+[Ru_3(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}]^-$ (L = amine) depends on the basicity of the amine. In the group NH_3, NH_2Et, $NHEt_2$, NEt_3 the reactivity follows the order $NEt_3 > NHEt_2 > NH_2Et > NH_3$. Only in the case of NH_2Et is the reaction slow enough to allow the detection of an intermediate species analogous to **IA** (^1H NMR: −16.50 ppm for the bridging hydride and −11.81 ppm for the terminal one). On the other hand, the less basic aniline reacts only at higher temperature, thus preventing the detection of the intermediate species. The formation of simple adducts between **I** and amines then appears strongly dependent upon a fine-tuning between the nitrogen atom basicity and the ability of the system to give rise to multiple interactions between the entering amine and the other ligands on the triruthenium surface.

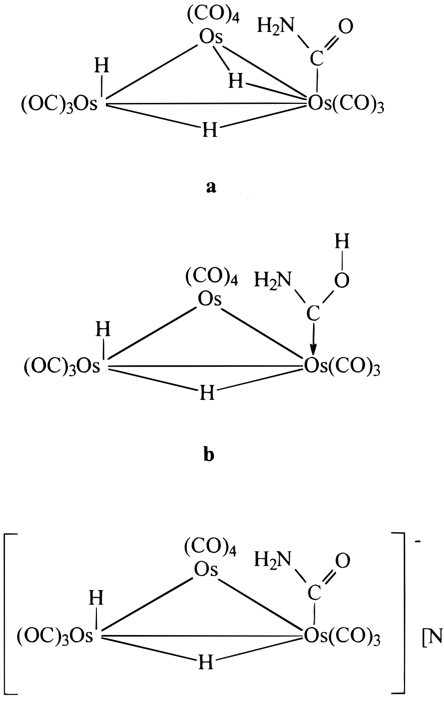
Low-Temperature Reaction of II with NH_3 and Related Amines. As recently shown,[6] **I** displays a bridging carbonyl ligand, whereas **II** possesses all terminal carbonyl groups.[7] In light of the results reported above for $Ru_3H(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}$, it was interesting to assess the behavior of $Os_3H(\mu\text{-}H)(CO)_{11}$ with NH_3.

When 500 Torr of NH_3 is added to a CD_2Cl_2 solution of **II** at 183 K, the **IIA** derivative is immediately formed.

Its ^1H NMR spectrum (CD_2Cl_2, 183 K) shows four equally intense signals at 8.0, 6.95, −10.83, and −19.9 ppm, respectively. When $^{15}NH_3$ is used, the two low-field signals appear as doublets with $^1J_{^{15}N,^1H}$ values of 90.1 and 80.0 Hz, respectively.

Ten ^{13}CO signals (which account for 11 carbonyl groups) are observed in the ^{13}C NMR spectrum (CD_2Cl_2, 183 K, Figure 2) at 189.3 ($^2J_{^{13}C,^{13}C} = 34.3$ Hz), 187.9 ($^2J_{^{13}C,^{13}C} = 34.4$ Hz), 187.1 (2 CO), 181.8 ($^2J_{^{13}C,^1H_{term}} = 25.6$ Hz), 178.9, 176.8, 175.6, 175.3, 174.2, and 173.1 ($^2J_{^{13}C,^1H_{bridge}} = 19.9$ Hz) ppm, respectively. The detection of a large two-bond coupling between an equatorial carbonyl and the bridging hydride suggests the occurrence of a strong asymmetry in the layout of the latter ligand along the Os−Os bond.

Chart 3



a

b

c

The ^{15}N NMR spectrum (CD_2Cl_2, 183 K) consists of a doublet of doublets centered at −231.2 ppm ($^1J_{^{15}N,^1H} = 80$ Hz, 90.1 Hz) in addition to the free $^{15}NH_3$ signal at −376.2 ppm. Unexpectedly, the latter signal appears as a broad singlet in the proton-coupled spectrum.

Under lower ammonia pressure (200 Torr) at the same temperature, another species (**IIA′**) can be detected, which slowly evolves to **IIA**. The **IIA′** spectroscopic properties suggest that it is an isomer of **IIA**. In fact, its ^1H NMR spectrum (CD_2Cl_2, 183 K) shows four signals at 6.35 (1H, $^1J_{^{15}N,^1H} = 80.5$ Hz), 5.87 (1H, $^1J_{^{15}N,^1H} = 86.4$ Hz), −9.7 (1H), and −18.2 (1H) ppm, respectively. Although several carbonyl resonances can be detected, the low yield of **IIA′** does not allow a complete assignment of its ^{13}C NMR spectrum. A doublet of doublets centered at −234.0 ppm ($^1J_{^{15}N,^1H} = 80.5$, 86.4 Hz) appears in the proton-coupled ^{15}N NMR spectrum.

The ^1H absorptions in the range 5.8−8.0 ppm together with the $^1H-^{15}N$ coupling pattern for either **IIA** or **IIA′** strongly suggest that the attack of NH_3 at $Os_3H(\mu\text{-}H)(CO)_{11}$ leads to the formation of a carbamoyl-type arrangement. Since the ^{13}C resonance for such an arrangement is expected to be found in the 170−180 ppm range,[11] it follows that one of the observed ^{13}C signals could be assigned to the carbamoyl functionality. On the basis of these findings, one may envisage three possible structures for a carbamoyl-containing system (Chart 3).

Structure **a** can be discarded, because three hydride resonances should be observed for it. On the other

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(11) Mann, B. E.; Taylor, B. F. In *^{13}C NMR Data for Organometallic Compounds*; Academic Press: London.

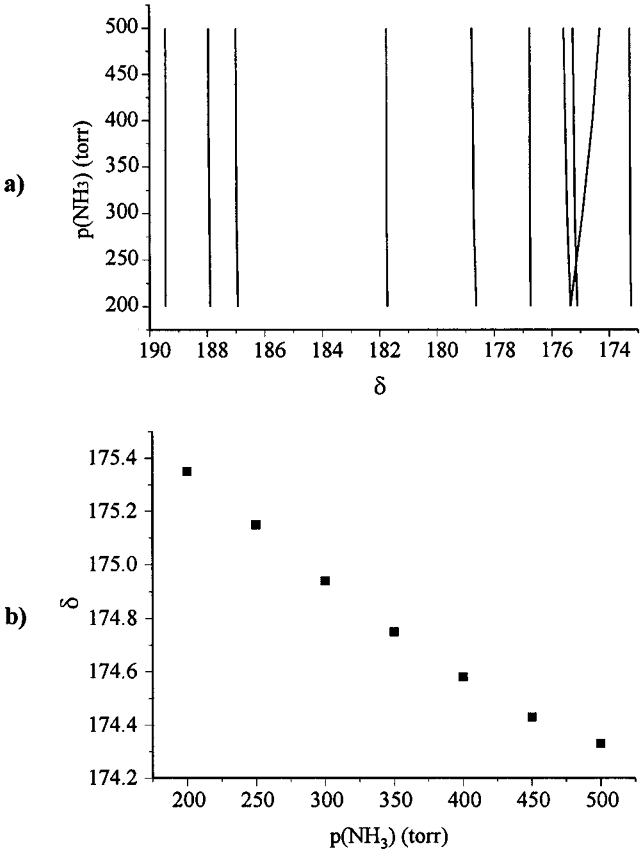
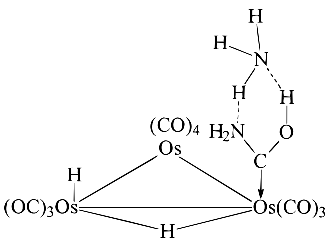


Figure 3. (a) Effect of the ammonia pressure upon the ^{13}C chemical shifts of **IIA**. (b) Variation of the carbamoyl carbon chemical shift.

Chart 4



d

hand, to support the occurrence of a **b**-type species one would need to observe the OH resonance, but we were unable to detect such a signal. Eventually, if structure **c** was the one occurring, it would display the NH_4^+ resonances in the ^1H and ^{15}N NMR spectra, but this is not the case.

More insight into the assignment of a structure to **IIA** could be obtained by the observation that a change in the ammonia pressure causes a selective effect on one ^{13}CO resonance of **IIA**, whose chemical shift goes from 175.4 to 174.3 ppm as the ammonia pressure increases from 200 to 500 Torr (Figure 3). Almost no effect is detected on the remaining 10 CO resonances.

On the basis of these considerations one may assign to **IIA** (and **IIA′**) a structure **d**, intermediate between **b** and **c**, i.e. an ion pair in fast exchange with free ammonia (Chart 4), and assign the resonance at 174.3/175.4 ppm to the carbamoyl carbon.

The occurrence of such a structure would account both for the lack of observation of any OH signal (i.e. it scrambles with the three protons on the NH_3 molecule) and for the fact that the ^1H and ^{15}N NMR signals for free ammonia appear invariably as broad singlets. Interestingly, a **d**-type arrangement was suggested some years ago to account for the 2:1 stoichiometry found for adducts formed in the reaction between $Fe(CO)_5$ and primary and secondary amines.[12]

Now, the structural difference between **IIA** and **IIA′** is based only on which carbonyl has undergone the ammonia attack.

As one goes from NH_3 to NH_2Et and $NHEt_2$, the reactivity increases, as expected on the basis of the increased nitrogen atom basicity. The ^1H NMR spectra (CD_2Cl_2, 183 K) of the formed **IIA**-type intermediates show absorptions in the hydride region at −10.53 and −19.87 ppm in the case of NH_2Et and at −9.67 and −19.04 ppm in the case of $NHEt_2$. Conversely, NEt_3 does not react at all, even at 298 K. This fact might suggest that a necessary requisite for promoting the reactions with **II** is the presence on the amine nitrogen atom of at least one proton, which can be transferred to the carbonyl oxygen atom to form the intermediate carbamoyl functionality. Anyway, another factor that may be considered to account for the lack of nucleophilic attack at the carbonyl moiety is the increased strain of NEt_3.

Conclusions

In summary, it is worth noting that the reactions of NH_3 with **I** and **II** at low temperature lead to kinetic products of the same molecular formula, corresponding to the addition of the entering ligand to the cluster. In **IA** the ammonia maintains its wholeness, whereas in the **IIA/IIA′** isomers one hydrogen is transferred from NH_3 to an oxygen atom to form an O−H bond. In principle, H_2 elimination from **IIA/IIA′**-type structures might be possible, leading to the formation of a μ-η^2-formamido cluster analogous to that reported from the reaction of dimethylamine with $Ru_3(CO)_{12}$.[3] We have no evidence for the occurrence of this transformation: the **IIA/IIA′** species behave like **IA** and favor the formation of $[NH_4]^+[Os_3(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}]^-$.

The lack of any reaction between NH_3 and $M_3(CO)_{12}$ (M = Ru, Os) even at room temperature[13] could be explained by a reduced electrophilicity of the carbonyl carbon atoms in these compounds with respect to the $M_3H(\mu\text{-}H)(CO)_{11}$ species. Nevertheless, if the electrophilicity difference was so important in determining the reactivity with NH_3, $Ru_3H(\mu\text{-}H)(CO)_{11}$ should react more easily than $Os_3H(\mu\text{-}H)(CO)_{11}$, due to the presence of the bridging carbonyl (whose carbon atom is more electrophilic than that of a terminal carbonyl), but this is not the case. Since hydride ligands have been shown to be able to form hydrogen bonds,[14] we think that the formation of such interactions between the entering NH_3 (or amine) molecule and the hydride ligands may also

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(12) (a) Edgell, W. F.; Bulkin, B. J. *J. Am. Chem. Soc.* **1966**, *88*, 4839. (b) Miller, J. R.; Podd, B. D.; Sanchez, M. O. *J. Chem. Soc., Dalton Trans.* **1980**, 1461.

(13) Aime, S.; et al. Unpublished results.

(14) (a) Richardson, T. B.; de Gala, S.; Crabtree, R. H.; Siegbahn, P. E. M. *J. Am. Chem. Soc.* **1995**, *117*, 12875. (b) Crabtree, R. H.; Siegbahn, P. E. M.; Eisenstein, O.; Rheingold, A. L.; Koetzle, T. F. *Acc. Chem. Res.* **1996**, *29*, 348. (c) Aime, S.; Gobetto, R.; Valls, E. *Organometallics* **1997**, *16*, 5140.

play a role in the early reaction steps, perhaps facilitating the NH_3 (or amine) approach to the clusters.

Experimental Section

All solvents were stored over molecular sieves and purged with nitrogen before use.

I and **II** were prepared according to the published methods.[6,15] ^{13}CO-enriched samples were synthesized by using ^{13}C-enriched (about 40%) $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$, obtained by direct exchange of ^{13}CO (300 Torr) with $M_3(CO)_{12}$ (200 mg) in cyclohexane at 343 K and in *n*-octane at 393 K, respectively, for 3 days in 250 mL sealed vials.

^{13}CO (99% enriched) and $^{15}NH_3$ (99.9% enriched) were purchased from EURISO-TOP (Saint Aubain, France); $^{14}NH_3$ was purchased from SIAD (Bergamo, Italy).

For the reactions with ammonia, 0.6 mL of a 2.7×10^{-2} mM solution of **I** or **II** were transferred into 5 mm resealable NMR tubes having a total volume of 3 mL. The solutions were frozen, the air was pumped off, and the desired amount of NH_3 was added. The reaction mixtures were then allowed to reach 183 K inside the NMR spectrometer. For the reactions with substituted amines (10-fold excess) a similar procedure was used.

The $[LH]^+[M_3(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}]^-$ (M = Ru, Os; L = amine) compounds were obtained by carrying out the reactions at 298 K. The solutions containing these products were then evaporated. The salts were recrystallized from methanol at 200 K, isolated as pure compounds, washed with methanol, and dried under vacuum (yield 62−79%). They were characterized on the basis of the IR (CH_3CN solutions) and NMR (CD_2Cl_2 solutions, 183 K) spectra and by elemental analysis.

M = Ru, L = NH_3: ^{1}H, δ −12.98; ^{13}C, δ 189.9 (2C), 196.1 (2C), 199.2 (2C, $^2J_{^{13}C,^1H} = 13.8$ Hz), 201.5 (2C), 208.2 (1C), 208.8 (1C), 289.8 (1C); IR (ν_{CO}, cm^{-1}), 2074 (vw), 2017 (vs), 1985 (s), 1705 (w), 1948 (m). Anal. Found: C, 20.71; H, 0.65; N, 2.07. Calcd for $C_{11}H_5NO_{11}Ru_3$: C, 20.96; H, 0.80; N, 2.22.

M = Ru, L = NH_2Et: ^{1}H, δ −13.00; IR (ν_{CO}, cm^{-1}), 2074 (vw), 2017 (vs), 1986 (s), 1705 (w), 1947 (m). Anal. Found: C, 23.93; H, 1.33; N, 2.21. Calcd for $C_{13}H_8NO_{11}Ru_3$: C, 23.75; H, 1.23; N, 2.13.

M = Ru, L = $NHEt_2$: ^{1}H, δ −13.24; IR (ν_{CO}, cm^{-1}), 2076 (vw), 2016 (vs), 1985 (s), 1710 (w), 1945 (m). Anal. Found: C, 26.39; H, 1.90; N, 2.13. Calcd for $C_{15}H_{12}NO_{11}Ru_3$: C, 26.28; 1.76; N, 2.04.

M = Ru, L = NEt_3: ^{1}H, δ −13.11; IR (ν_{CO}, cm^{-1}), 2074 (vw), 2015 (vs), 1984 (s), 1706 (w), 1947 (m). Anal. Found: C, 28.78; H, 2.17; N, 2.01. Calcd for $C_{17}H_{15}NO_{11}Ru_3$: C, 28.62; H, 2.26; N, 1.96.

M = Os, L = NH_3: ^{1}H, δ −14.20; ^{13}C, δ 172.2 (2C), 175.5 (2C), 179.5 (2C, $^2J_{^{13}C,^1H} = 13.0$ Hz), 181.1 (1C), 182.9 (1C), 183.4 (2C), 274.6 (1C); IR (ν_{CO}, cm^{-1}), 2039 (w), 2019 (s), 1998 (s), 1950 (m), 1662 (w). Anal. Found: C, 14.89; H, 0.70; N, 1.66. Calcd for $C_{11}H_5NO_{11}Os_3$: C, 14.72; H, 0.56; N, 1.56.

M = Os, L = NH_2Et: ^{1}H, $\delta = -14.24$; IR (ν_{CO}, cm^{-1}), 2038 (w), 2020 (s), 1998 (s), 1952 (ms), 1661 (w). Anal. Found: C, 16.79; H, 0.80; N, 1.41. Calcd for $C_{13}H_8NO_{11}Os_3$: C, 16.88; H, 0.87; N, 1.51.

M = Os, L = $NHEt_2$: ^{1}H, $\delta = -14.36$; IR (ν_{CO}, cm^{-1}), 2040 (w), 2018 (s), 1997 (s), 1951 (m), 1662 (w). Anal. Found: C, 18.75; H, 1.21; N, 1.35. Calcd for $C_{15}H_{12}NO_{11}Os_3$: C, 18.91; H, 1.27; N, 1.47.

The NMR spectra were obtained on a JEOL EX-400 instrument, operating at 399.65, 100.25, and 40.40 MHz for ^{1}H, ^{13}C, and ^{15}N observation, respectively. The scale reference for ^{15}N measurements was given with respect to nitromethane (δ 0).

The assignments of the ^{13}C−^{1}H couplings to terminal vs bridging hydrides were done by selective decouplings.

The nonselective inversion recovery pulse sequence[16] was used to measure the T_1 values.

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