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Reactions of Secondary Amines with Triosmium Decacarbonyl Bis(acetonitrile): Room-Temperature C–H Activation and Transalkylation

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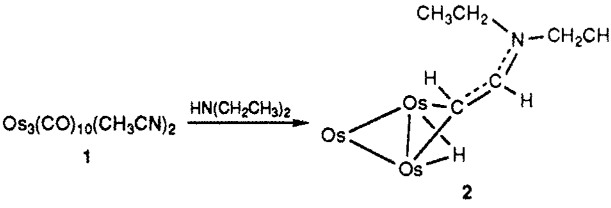
Summary: The reactions of secondary aliphatic amines with triosmium decacarbonyl bis(acetonitrile) yield a range of trinuclear products that result from transalkylation and/or carbon–hydrogen bond activation of the alkyl groups on the amine. The nature of the products obtained is remarkably sensitive to the structure and steric requirements of the amine employed.

Although there are numerous examples in the literature of triosmium clusters capped or bridged with nitrogen-containing ligands, there have been few systematic investigations of the reactivity of triosmium clusters with a homologous series of simple aliphatic amines.[1-4] Cleavage of both nitrogen–hydrogen bonds[3] and carbon–hydrogen bonds in the ligand, at 20–80 °C, has been observed in these triosmium systems.[1] Recently, formation of an amine-stabilized η^1-carbene has been reported,[2] and we have reported trinuclear products resulting from carbon–nitrogen bond cleavage and carbon–carbon bond coupling in the reaction of $Ru_3(CO)_{12}$ with tertiary amines at 70–80 °C.[5-7]

We have begun a systematic investigation of the reactions of $Os_3(CO)_{10}(CH_3CN)_2$[8] (1) with secondary aliphatic amines and note a remarkable sensitivity of the type of product obtained, depending on the nature of the secondary amine used. We have observed both α- and β-carbon–hydrogen bond activation and α-carbon–hydrogen bond activation only, as well as transalkylation, all in the temperature range 25–45 °C.

Thus, the reaction of diethylamine with 1 in CH_2Cl_2 for 15 h at 25 °C or in C_6H_6 for 6 h at 40–45 °C (eq 1) gives one major amine-containing trinuclear product, $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}\eta^1\text{-CHCHN}(CH_2CH_3)_2)$ (2), in 24% and 22% yield, respectively. Compound 2 was previously reported to be the major product from the reaction of 1 with triethylamine in refluxing benzene (36%) along with $H_2Os_3(CO)_{10}$ (30%).[9] The formation of 2 from diethylamine thus constitutes an unusual low-temperature transalkylation. The moderate yields realized for 2 are in part due to the formation of $(\mu\text{-H})(\mu\text{-OH})Os_3(CO)_{10}$[10] in 10% yield from the competitive reaction of 1 with traces of water that are retained by 1 after silica gel chromatographic purification.[11] Only one other very minor product was isolated in <5% yield, which has not yet been completely characterized. Other workers have observed related transalkylation[12] and carbon–nitrogen bond cleavage[13] in



(1)

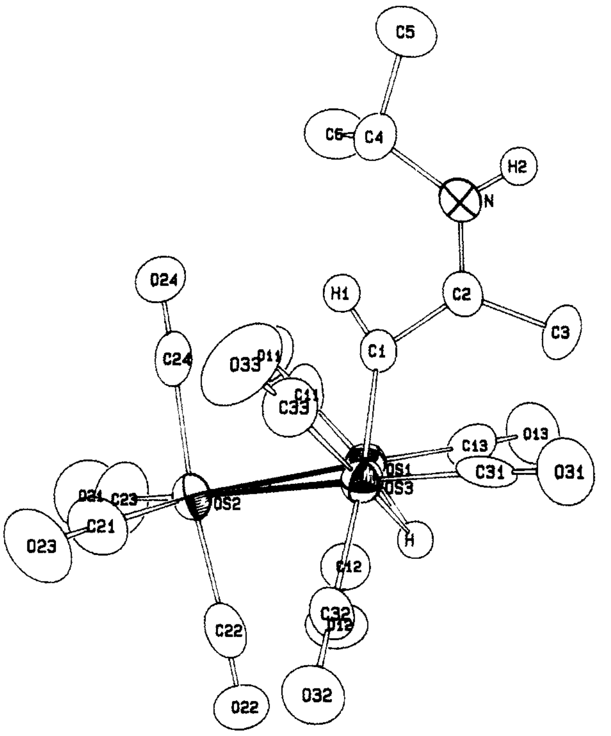


Figure 1. ORTEP drawing of $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}\eta^1\text{-CHC}(CH_3)N(H)(CH(CH_3)_2)$ (3) showing 30% probability ellipsoids. Selected distances (Å) and bond angles (deg): Os(1)–Os(2) = 2.870 (1), Os(2)–Os(3) = 2.868 (1), Os(1)–Os(3) = 2.787 (1), Os(1)–C(1) = 2.20 (2), Os(3)–C(1) = 2.19 (2), C(1)–C(2) = 1.45 (2), C(2)–N = 1.30 (2); C(1)–C(2)–N = 121 (1). The positions of the hydrogen atoms shown are calculated by using the program HYDRO, for the hydrogens bound to nitrogen and carbon 1, and the program HYDEX, for the hydride.[15]

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[1] Deeming, A. J. *Adv. Organomet. Chem.* **1986,** *26,* 1.

[2] Adams, R. D.; Chen, G.; Tanner, J. T.; Yin, J. *Organometallics* **1989,** *8,* 2493 and references therein.

[3] Diztel, S. J.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1987,** 1293.

[4] Deeming, A. J.; Minassian, H.; Arce, A. J.; De Sanctis, Y.; Hardcastle, K. I. *J. Organomet. Chem.* **1989,** *368,* 119.

[5] Rosenberg, E.; Aime, S.; Gobetto, R.; Padovan, F.; Botta, M.; Gellert, R. *Organometallics* **1987,** *6,* 2074.

[6] Rosenberg, E.; Hajela, S.; Hardcastle, K. I.; McPhillips, T.; Day, M. W.; Gellert, R. W.; Botta, M.; Gobetto, R.; Milone, L.; Osella, D. *Organometallics* **1990,** *9,* 913.

[7] Rosenberg, E.; Hardcastle, K. I.; Day, M.; Hajela, S.; Wolf, E.; Milone, L.; Gobetto, R. Abstracts, 1989 Pacifichem Meeting, Honolulu, Hawaii; Dec 17–22, 1989; American Chemical Society: Washington, DC, 1989; also submitted for publication.

[8] (a) Johnson, B. F. G.; Lewis, J.; Pippard, D. A. *J. Chem. Soc., Dalton Trans.* **1981,** 407. (b) Arce, A. J.; De Sanctis, Y.; Deeming, A. J. *J. Organomet. Chem.* **1985,** *295,* 365.

[9] (a) Shapley, J. R.; Tachikawa, M.; Churchill, M. R.; Lashewycz, R. A. *J. Organomet. Chem.* **1978,** *162,* C39. (b) Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* **1979,** *18,* 849. Our NMR and spectra data for 2 are identical with those reported by Shapley et al.

[10] Johnson, B. F. G.; Lewis, J.; Kilty, O. A. *J. Chem. Soc. A* **1968,** 2859.

[11] Amines were distilled from sodium directly before use after predrying with potassium hydroxide. Methylene chloride was distilled from phosphorus pentoxide and benzene from sodium benzophenone ketyl directly before use. Formation of $(\mu\text{-H})(\mu\text{-OH})Os_3(CO)_{10}$ has been previously reported in the reactions of 1 with oxygen-containing ligands: Kabir, S.E. Ph.D. Thesis, University College, London, University of London, 1986. See also: Ditzel, E. J.; Geomez-Sal, M. P.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1987,** 1623.

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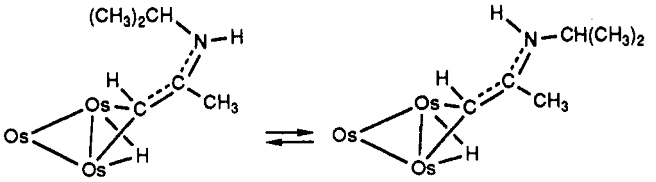
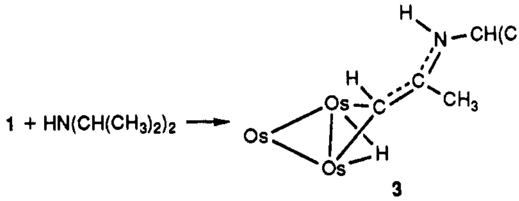
Scheme I. Proposed Isomers for Compound 3



the reactions of tertiary amines with triosmium clusters, but only at elevated temperatures (125–143 °C).

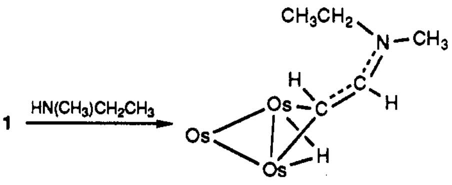
In our previous work with $Ru_3(CO)_{12}$ and tertiary amines we noted that relatively bulky amines such as ethyldiisopropylamine precluded the carbon–nitrogen bond cleavage processes associated with the reaction of $Ru_3(CO)_{12}$ and triethylamine and we thought that the use of a relatively bulky secondary amine might have a similar blocking effect on the apparent coupling reaction represented in eq 1. Indeed, when 1 is treated with diisopropylamine for 40 h in CH_2Cl_2 at 25 °C or for 8 h in C_6H_6 at 40–45 °C, the major product is $(\mu\text{-H})(\mu\text{-}\eta^1\text{-CHC(CH}_3\text{)NHCH(CH}_3)_2)\text{-}Os_3(CO)_{10}$ (**3**) in 29% and 31% yield, respectively (eq 2). The only other products were $(\mu\text{-H})(\mu\text{-OH})Os_3(CO)_{10}$ (~10%) and $H_2Os_3(CO)_{10}$ (<5%).



3 (2)

The general structure of **3** could be inferred from ^1H NMR data,[14] but since it exists as two isomers in solution (Scheme I) and is a novel secondary analogue of **2**, a solid-state structural investigation was undertaken. The overall structure of the bridging ligand appears to be identical in **2** and **3** (Figure 1). The geometry around the C(1)–C(2) bond in **2** is trans, as evidenced from the large three-bond coupling (13.9 Hz) observed in the ^1H NMR spectrum.[9] Rotation around this bond is slow on the NMR time scale up to 70 °C, suggesting considerable double-bond character. In **3** we cannot observe an analogous trans coupling due to the presence of the methyl group on C(2), but the location of the methyl group, the observation of the same size three-bond coupling between the hydride and the hydrogen on C(1) in **2** and **3** (2.5–3.0 Hz), and the almost identical C(1)–C(2) bond lengths (1.42 (3) Å in **2** and 1.45 (2) Å in **3**) all point to them having the same geometry around the C(1)–C(2) bond. The C(2)–N bond lengths are also quite similar (1.28 (3) Å in **2** and 1.30 (2) Å in **3**). The two isomers of **3** observed in solution probably differ in their relative orientation around the carbon–nitrogen double bond (Scheme I) rather than the C(1)–C(2) bond, where cis–trans isomers would be expected to be more different in energy as for **2**. These isomers of **3** do not interconvert on the NMR time scale up to +70 °C.

It is tempting to propose that the structure of **3** represents the direct precursor to the coupling product **2**. Adams et al. have recently observed a similar transamination in a face-capping analogue of **2**.[16] However, neither **2** nor **3** undergoes such transaminations when treated with diethylamine or dimethylamine.[17] It appears that either the presence of the methyl group on C(2) in **3** or the presence of two alkyl groups on nitrogen in **2** sterically hinders nucleophilic displacement at this carbon. This proposed reaction pathway was tested by treating 1 with a mixture of an excess of dimethylamine and diethylamine (5:1 relative to 1) in CH_2Cl_2 at room temperature. Unfortunately, 1 decomposes to an intractable baseline residue in this mixture or in the presence of dimethylamine alone. Addition of diethylamine to 1 followed by immediate addition of dimethylamine led to lower yields of **2** and decomposition. We have found, however, that one of the expected crossover products is obtained in the reaction of 1 with methylethylamine, which gives $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}\eta^1\text{-CHCHN(CH}_3\text{)CH}_2\text{CH}_3)$ (**4**) as a mixture of two isomers in 15% yield in CH_2Cl_2 at room temperature[18] (eq 3).



4 (3)

Three other minor products were obtained (<5% each), which are currently undergoing characterization, but their ^1H NMR spectra indicate that none of these products are structurally related to **2** or **3**.

In sharp contrast to what was observed with diethylamine and diisopropylamine, the reaction of 1 with pyrrolidine leads to a major product in which only α-carbon–hydrogen bonds are activated. Thus, reaction of 1 with pyrrolidine at 40–45 °C in benzene for 8 h yields three products, $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}\eta^1\text{-}\overline{NCH_2CH_2CH_2CH_2})$ (**5**),

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(12) Adams, R. D.; Kim, H.; Wang, S. *J. Am. Chem. Soc.* **1985**, *107*, 6107.

(13) Yin, C. C.; Deeming, A. J. *J. Organomet. Chem.* **1977**, *133*, 123.

(14) Spectral data for **3**: IR (ν(CO) in hexane) 2091 m, 2045 vs, 2034 s, 2010 vs, 1999 s, 1993 s, 1978 w, 1963 m, 1955 m, 1943 vw cm^{-1}; ^1H NMR (in $CDCl_3$) two isomers, isomer a (60%) δ 6.62 (br, 1 H), 4.86 (d, H, J_{H-H} = 3.0 Hz), 3.85 (spt, 1 H, J_{H-H} = 7.2 Hz), 2.04 (s, 3 H), 1.31 (d, 3 H, J_{H-H} = 7.2 Hz), 1.27 (d, 3 H, J_{H-H} = 7.2 Hz), −16.19 (d, 1 H, J_{H-H} = 3.0 Hz), isomer b (40%) δ 6.22 (br, 1 H), 5.12 (d, 1 H, J_{H-H} = 2.4 Hz), 3.85 (spt, 1 H, J_{H-H} = 7.2 Hz), 2.00 (s, 3 H), 3.1 (d, 3 H, J_{H-H} = 7.2 Hz), 1.27 (d, 3 H, J_{H-H} = 7.2 Hz), −16.32 (d, 1 H, J_{H-H} = 3.0 Hz). Satisfactory elemental analyses (C, H, N) have been obtained.

(15) X-ray diffraction data were collected on an Enraf-Nonius CAD4 diffractometer at room temperature with use of Mo Kα radiation. Calculations were performed on a Digital Equipment Corp. MicroVAXII computer using SHELX-86 and the SDP/VAX system of programs. The data were corrected for absorption. Crystals of **3** were grown from 5:1 hexane/dichloromethane at −20 °C. Compound **3** crystallizes in the monoclinic crystal system: space group $P2_1/n$, a = 12.995 (4) Å, b = 10.320 (3) Å, c = 16.932 (3) Å, β = 104.80 (1)°, V = 2196 (1) $Å^3$, Z = 4, ρ_{calc} = 3.00 g/cm^3. The structure was solved by the Patterson heavy-atom method and refined (3991 reflections) to final values of the residuals R = 0.055 and R_w = 0.072. The positions of the hydrogen atoms and the hydrides were calculated by using the program HYDRO (Frenz, B. A. The Enraf-Nonius CAD4SDP-A Real-time System for Concurrent X-Ray Data Collection and Crystal Structure Determination. In *Computing in Crystallography*; Schenk, H., Ollthof-Hazelkamp, R.; von Konigsveld, H.; Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp. 64–71) and HYDEX (Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2509), respectively.

(16) Adams, R. D.; Turner, J. T. *Organometallics* **1988**, *7*, 2241.

(17) Comounds **2** and **3** were subjected to reflux at 80–100 °C in hydrocarbon solvents for 4 h in the presence of excess dimethylamine and diethylamine, respectively.

(18) Spectral data for **4**: IR (ν(CO) in cyclohexane) 2090 w, 2057 w, 2045 s, 2035 m, 2009 s, 1992 s, 1986 m, 1977 w, 1963 s cm^{-1}; ^1H NMR (in $CDCl_3$) two isomers, isomer a (70%) δ 7.06 (d, 1 H, J_{H-H} = 14.5 Hz), 4.66 (dd, 1 H, J_{H-H} = 14.5, J_{H-H} = 2.5 Hz), 3.35 (q, 2 H, J_{H-H} = 7.4 Hz), 2.93 (s, 3 H), 1.29 (t, 3 H, J_{H-H} = 7.4 Hz), −16.82 (d, 1 H, J_{H-H} = 2.5 Hz), isomer b (30%) δ 7.05 (d, H, J_{H-H} = 14.5 Hz), 4.70 (dd, 1 H, J_{H-H} = 14.5 Hz, J_{H-H} = 2.5), 3.35 (q, 2 H, J_{H-H} = 7.4 Hz), 3.03 (s, 3 H), 1.29 (t, 3 H, J_{H-H} = 7.4 Hz), −16.73 (d, 1 H, J_{H-H} = 2.5 Hz). Satisfactory elemental analysis for this compound was obtained. Three other minor products in addition to $H_2Os_3(CO)_{10}$ and $(\mu\text{-H})(\mu\text{-OH})Os_3(CO)_{10}$ were isolated in about 5% yield each, and their characterization is currently underway.

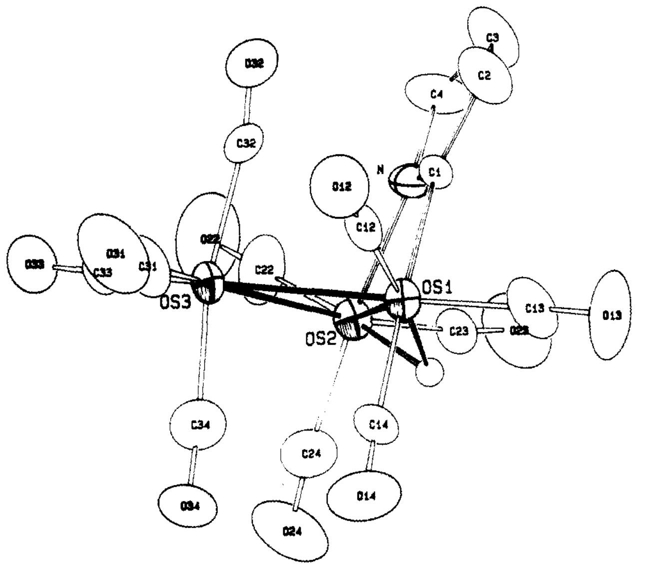
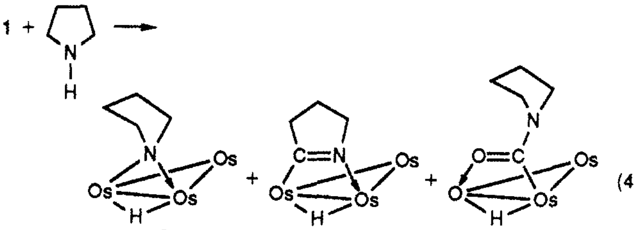


Figure 2. ORTEP drawing of $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-}\overline{\text{C=NCH}_2\text{CH}_2\text{CH}_2})$ (6) showing the 50% probability ellipsoids. Selected distances (Å): Os(1)–Os(2) = 2.930 (1), Os(2)–Os(3) = 2.868 (1), Os(3)–Os(1) = 2.870 (1), Os(1)–C(1) = 2.14 (1), Os(2)–N = 2.12 (1), C(1)–N(1) = 1.25 (2). The position of the hydride shown is calculated by using the program HYDEX.[15]

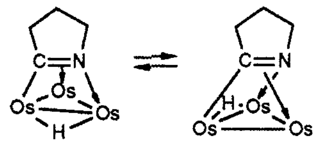
$(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-}\overline{\text{C=NCH}_2\text{CH}_2\text{CH}_2})$ (6), and $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-O=}\overline{\text{CNCH}_2\text{CH}_2\text{CH}_2\text{CH}_2})$ (7), in 7%, 50%, and 3% yields, respectively (eq 4).[19] Compounds of



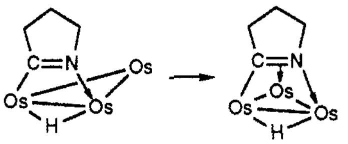
5 6 7 (4)

structural types 5 and 7 have been previously reported.[20,21] A solid-state structural investigation of 6 revealed that the organic ligand is η^2-coordinated to the Os–Os edge bridged by the hydride through a metal–carbon σ bond and a two-electron donor bond from the nitrogen (Figure 2).[22]

Scheme II. Fluxional Process in Compound 6a

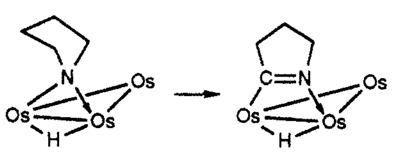


The carbon–nitrogen bond length of 1.25 (2) Å is typical of carbon–nitrogen double bonds in the closely related triosmium complexes $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-HC=NR})$.[23] Refluxing 6 in octane for 24 h yields $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-}\overline{\text{C=NCH}_2\text{CH}_2\text{CH}_2})$ (6a) quantitatively (eq 5). Com-



6 6a (5)

pound 6a is an osmium analogue of the previously reported $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-CH}_3\text{C=NCH}_2\text{CH}_3)$[24] and exhibits the same fluxional behavior as its ruthenium analogue (Scheme II).[25] Interestingly, the estimated activation barrier in 6a for this process is very similar to that of its ruthenium analogue ($\Delta G^{\ddagger}_{293}$ = 56 ± 2 kJ/mol for 6a and $\Delta G^{\ddagger}_{213}$ = 42 ± 2 kJ/mol for $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\text{CH}_3\text{C=NCH}_2\text{CH}_3)$.[24] Even more interesting is the fact that only upon reflux in heptane for 4 h is 5 converted quantitatively to 6, thus suggesting that at lower temperatures N–H and C–H activation are competitive processes but that 5 is not a direct precursor to 6 (eq 6). Compounds of structural type 7 have been previously shown to convert slowly to structural type 5.[21] We have also found that 7 converts to 5 after refluxing in octane for 12 h. The formation of 7 is somewhat puzzling with regard to the source of the additional 1 mol of carbon monoxide. It is possible this compound formed from minor amounts of $\text{Os}_3(\text{CO})_{11}(\text{CH}_3\text{CN})$ in our preparation of 1 or from carbon monoxide available from cluster degradation products. Independent experiments with $\text{Os}_3(\text{CO})_{11}(\text{CH}_3\text{CN})$ verify this point, since 7 is ob-



5 6 (6)

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(19) Spectral data for 5: IR (ν(CO) in cyclohexane) 2099 w, 2057 vs, 2046 s, 2015 vs, 2002 s, 1982 s, 1972 w cm^{-1}; 80-MHz ^{1}H NMR (in CDCl$_3$) δ 3.84 (t, 2 H, $J_{\text{H-H}}$ = 7.2 Hz), 3.26 (t, 2 H, $J_{\text{H-H}}$ = 7.2 Hz), 1.84 (m, 4 H), −13.69 (s, 1 H). Spectral data for 6: IR (ν(CO) in cyclohexane) 2102 m, 2060 vs, 2048 s, 2021 s, 2002 vs, 1998 sh, 1988 s, 1974 w cm^{-1}; 80-MHz ^{1}H NMR (in CDCl$_3$) δ 3.57 (m, 2 H), 2.46 (m, 2 H), 1.77 (m, 2 H), −15.33 (s, 1 H). Spectral data for 7: IR (ν(CO) in cyclohexane) 2103 w, 2062 vs, 2050 s, 2019 s, 2007 vs, 1987 m, 1971 w cm^{-1}, ν(CO) for μ-η^2-acyl 1450 m cm^{-1} (KBr); 400-MHz ^{1}H NMR δ 3.56 (m, 1 H), 3.48 (m, 1 H), 3.21 (m, 2 H), 1.70–1.95 (m, 4 H), −13.89 (s, 1 H). Satisfactory elemental analyses were obtained for all three compounds.

(20) Specific analogues of 5 are $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-N(H)R})$. R = CH$_3$: Ditzel, S. J.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1987**, 1293. R = n-C$_4$H$_9$: Bryan, E. G.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1977**, 1328. We have completed a solid-state structural investigation of 5, which shows the structure to be as indicated in eq 4. This work is omitted here in the interest of brevity and will be reported separately.

(21) Specific analogues of 7 are $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-}\overline{\text{XCH=CHCH=CCO}})$ (X = O, N, S): Arce, A. J.; De Sanctis, Y.; Deeming, A. J. *J. Organomet. Chem.* **1986**, *311*, 371. $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{CONHCH}_3)$: Kaesz, H. D.; Knobler, C. B.; Andrews, M. A.; van Buskirk, G.; Szostak, R.; Strouse, C. E.; Lin, Y. C.; Mayr, A. *Pure Appl. Chem.* **1982**, *54*, 131. $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{OCNCH}_2\text{PhH})$: Azam, K. A.; Yin, C. C.; Deeming, A. J. *J. Chem. Soc., Dalton Trans.* **1978**, 1201.

(22) X-ray diffraction data were collected on an Enraf-Nonius CAD4 diffractometer at room temperature with use of Mo Kα radiation. Calculations were performed on a Digital Equipment Corp. MicroVAXII computer using SHELX-86 and the SDP/VAX system of programs. The data were corrected for absorption. Crystals of 6 were obtained from a saturated hexane/CH$_2$CH$_2$ solution at −20 °C. Compound 6 crystallized in the orthorhombic space group $P2_12_12_1$: a = 9.532 (2) Å, b = 12.199 (3) Å, c = 16.957 (4) Å, V = 1970 Å^3, Z = 4, and ρ_{calc} = 3.01 g/cm^3. The structure was solved by the Patterson heavy-atom method and was refined (2796 reflections) to final values of the residuals R = 0.045 and R_w = 0.049.

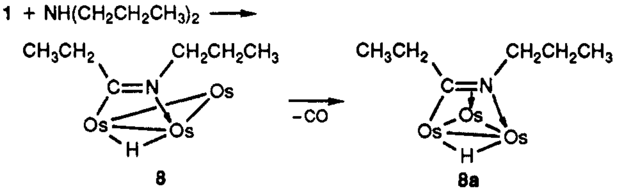
(23) Adams, R. D. *Acc. Chem. Res.* **1983**, *16*, 67.

(24) Aime, S.; Gobetto, R.; Padovan, F.; Botta, M.; Rosenberg, E.; Gellert, R. W. *Organometallics* **1987**, *6*, 2074.

(25) Spectral data for 6a: IR (ν(CO) in cyclohexane) 2089 m, 2063 vs, 2036 vs, 2011 vs, 1998 m, 1990 s, 1978 sh, 1964 w cm^{-1}; 400-MHz ^{1}H NMR (in CD$_2$Cl$_2$ at −40 °C (low-temperature limit)) δ 3.46 (two multiplets partially overlapping, 2 H), 3.10 (m, 1 H), 2.97 (m, 1 H), 2.10 (m, 1 H), 1.59 (m, 1 H), −17.96 (s, 1 H), (in CD$_2$Cl$_2$ at +40 °C (high-temperature limit)) δ 3.46 (t, 2 H, $J_{\text{H-H}}$ = 6.86 Hz), 3.05 (t, 2 H, $J_{\text{H-H}}$ = 6.83 Hz), 1.85 (t, 2 H, $J_{\text{H-H}}$ = 6.4 Hz).

tained as the only product at room temperature.

The reaction of di-*n*-propylamine with **1** yields none of the earlier products represented by **5** or **7** but only the analogue of **6** ($(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}CH_3CH_2C{=}NCH_2CH_2CH_3)$ (**8**) in 35% yield, which converts to **8a** quantitatively on thermolysis (eq 7).[26] Compound **8** is also obtained as the only product from the reaction of di-*n*-propylamine with $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}CHCH_2)$ (42% yield, refluxing benzene, 8 h). Compound **8a** also exhibits the fluxional behavior illustrated in Scheme II with an estimated barrier similar to that for **6a** ($\Delta G^{\ddagger}_{293} = 55 \pm 2$ kJ/mol). The fact that **6a** and **8a** and their ruthenium analogues exhibit relatively low barriers to the windshield-wiper motion of the μ_3-imino ligand compared to that for similar motions of μ_3-hydrocarbon ligands on triosmium and triruthenium clusters[27] points to the special lability of the hard nitrogen atom in these clusters.



8

8a

(7)

In summary, the reactions of **1** with secondary amines exhibited a high degree of sensitivity to the alkyl substituents on the amine, as evidenced by the completely different products obtained from pyrrolidine and di-*n*-propylamine versus diethylamine and diisopropylamine. In all cases, relatively rare room-temperature activation of aliphatic carbon–hydrogen bonds is observed.[28] Further studies on this alkyl group sensitivity and studies on the reactivity of complexes such as **6a** and **8a** are currently underway in our laboratories.

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Supplementary Material Available: A complete listing of bond distances and angles and tables of atomic coordinates and thermal parameters for **3** and **6** (13 pages); tables of structure factors for **3** and **6** (68 pages). Ordering information is given on any current masthead page.

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(26) Spectral data for **8**: IR (ν(CO) in hexane): 2100 m, 2057 vs, 2047 s, 2020 s, 2001 vs, 1998 sh, 1983 s, 1970 w cm^{-1}; 80-MHz ^1H NMR (in C_6D_6) δ 3.24 (m, 1 H), 2.78 (m, 1 H), 2.13 (m, 2 H), 1.17 (m, 2 H), 0.73 (t, 3 H, J_{H-H} = 7.6 Hz), 0.45 (t, 3 H, J_{H-H} = 7.3 Hz), −15.19 (s, 1 H). Spectral data for **8a**: IR (ν(CO) in cyclohexane): 2087 m, 2059 vs, 2035 vs, 2008 vs, 1994 m, 1986 s, 1977 sh, 1963 w cm^{-1}; 400-MHz ^1H NMR (at −40 °C (low-temperature limit)) δ 3.91 (m, 1 H), 2.94 (two partially overlapping multiplets, 2 H), 2.65 (m, H), 1.75 (m, 1 H), 1.43 (m, 1 H), 1.15 (t, 3 H, J_{H-H} = 7.4 Hz), 0.86 (t, 3 H, J_{H-H} = 7.4 Hz), −17.54 (s, 1 H). Satisfactory elemental analyses have been obtained.

(27) (a) Aime, S.; Gobetto, R.; Osella, D.; Milone, L.; Rosenberg, E. *Organometallics* **1982**, *1*, 640. (b) Rosenberg, E.; Bracker-Novak, J.; Gellert, R. W.; Aime, S.; Gobetto, R.; Osella, D. *J. Organomet. Chem.* **1989**, *365*, 163.

(28) For a recent example see: Zoet, R.; Van Koten, G.; Vrieze, K.; Jansen, J.; Goubitz, K.; Stam, C. H. *Organometallics* **1988**, *7*, 1564.