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# Nonrigidity in the Isomers of $Os_3(\mu\text{-}H)_2(CO)_9(CNBu^t)$. Structure of the Green Isomer

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Rapid heating of $HOs_3(\mu\text{-}H)(CO)_{10}(CNBu^t)$ in hexane produces $Os_3(\mu\text{-}H)_2(CO)_9(CNBu^t)$ (**1g**) as the green isomer. Further heating causes the green isomer to convert to the known red isomers (**1ra**, **1rb**). The structure of **1g** has been determined by X-ray crystallography: space group $P2_1/n$ with $a$ = 11.341 (2) Å, $b$ = 12.106 (2) Å, $c$ = 16.225 (2) Å, $\beta$ = 108.43 (1)°, $V$ = 2113.3 Å$^3$, $Z$ = 4; $R_1$ = 0.034, $R_2$ = 0.034 for 2044 reflections with $I > 2.5\sigma(I)$ having $2\theta \leq 50°$. It reveals a triangular $Os_3$ framework with one short Os–Os vector (Os(2)–Os(3) = 2.680 (1) Å) consistent with the presence of an $Os(\mu\text{-}H)_2Os$ unit; the other Os–Os bond lengths are both 2.812 (1) Å. In contrast to **1ra** and **1rb**, the $CNBu^t$ ligand in **1g** is bonded (in an axial site) to the osmium atom not associated with the bridging hydrides. The nonrigidity in the three isomers has been studied by variable-temperature $^1H$ and $^{13}C$ NMR spectroscopy. Changes occur in $^{13}C$ NMR spectra of **1g** in solution above −10 °C that are consistent with 3-fold rotation of the carbonyls of the $Os(CO)_3$ units; the hydride ligands and the carbonyls of the $Os(CO)_3(CNBu^t)$ grouping remain rigid during this process. Similar rearrangements, but with higher activation energies, occur in **1ra**. The exchange for the $Os(CO)_3$ unit has a slightly lower activation energy than that for the $Os(CO)_2(CNBu^t)$ unit. The latter rearrangement interconverts isomers **1ra** and **1rb**. Once again, the other ligands in the molecule remain rigid up to the temperature at which isomerization becomes significant on the NMR time scale.

## Introduction

One of the remarkable properties of organometallic cluster compounds is their stereochemical nonrigidity.[1,2] Numerous studies have described the mobility, as detected by NMR spectroscopy, of ligands such as carbonyl and hydride in clusters.[1,2] Studies on the nonrigidity of hydridoosmium carbonyl clusters have usually been restricted to those with single hydride bridges (i.e., $Os(\mu\text{-}H)Os$),[3] few being on clusters with the formally unsaturated $Os(\mu\text{-}H)_2Os$ unit.[4] This is because clusters with the latter unit are rare, and, furthermore, most of the compounds that contain this unit are symmetric and the hydride ligands are chemically equivalent (e.g., $Os_3(\mu\text{-}H)_2(CO)_{10}$,[5] $Os_3(\mu\text{-}H)_2(CO)_9(PPh_3)$[6]). For this reason, hydride exchange and many of the possible carbonyl exchanges cannot be detected in these molecules by NMR techniques.

It is known, however, that the inequivalent carbonyls associated with the $Os(\mu\text{-}H)_2Os$ unit of $Os_3(\mu\text{-}H)_2(CO)_{10}$ exchange on the NMR time scale.[7,8] From a study of the deuterium kinetic isotope effect on this exchange it was concluded that the hydride ligands were rigid during the carbonyl exchange.[9] Work from this laboratory has shown that the hydrides of the $Os(\mu\text{-}H)_2Os$ group of $Os_3(\mu\text{-}H)_3(CO)_9(SiPh_3)$ undergo mutual exchange and they also exchange at a slower rate with the hydride of the $Os(\mu\text{-}H)Os$ unit. This led to the suggestion that there may be hydride migration from a bridging position to the center of the cluster in this molecule.[4]

In a study unrelated to those concerned with the fluxional properties of osmium clusters, we had occasion to prepare $Os_3(\mu\text{-}H)_2(CO)_9(CNBu^t)$ (**1**) using the method of Adams and Golembeski (eq 1 and 2).[10] As originally

$$Os_3(\mu\text{-}H)_2(CO)_{10} + CNBu^t \rightarrow HOs_3(\mu\text{-}H)(CO)_{10}(CNBu^t) \tag{1}$$

$$HOs_3(\mu\text{-}H)(CO)_{10}(CNBu^t) \xrightarrow{\Delta} \underset{\mathbf{1}}{Os_3(\mu\text{-}H)_2(CO)_9(CNBu^t)} \tag{2}$$

reported and confirmed by us, **1** prepared by this method consists of a mixture of isomers that are red. It was, noticed by chance, however, that rapid heating of solutions of $HOs_3(\mu\text{-}H)(CO)_{10}(CNBu^t)$ initially turned green. Further investigation revealed that the green color is due to a third isomer of **1**. This in turn prompted the detailed study reported here of the nonrigid properties of the three isomers of **1**.

## Experimental Section

Unless otherwise stated, manipulations of starting materials and products were carried out under a nitrogen atmosphere with use of standard Schlenk techniques. Hexane was refluxed over potassium, distilled, and stored under nitrogen before use. Dichloromethane was treated similarly except that $P_2O_5$ was used as the drying agent. The starting material $Os_3(\mu\text{-}H)_2(CO)_{10}$ was prepared by a modification of the literature method.[11] Although the yield in our preparation (60–65%) is somewhat lower than that reported in the original preparation (73%), we find the yields are more consistent with use of our method. The preparation of $HOs_3(\mu\text{-}H)(CO)_{10}(CNBu^t)$ and the red isomers of $Os_3(\mu\text{-}H)_2(CO)_9(CNBu^t)$ has been described.[10,12] The $^{13}CO$-enriched com-

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[1] (a) Band, E.; Muetterties, E. L. *Chem. Rev.* **1978**, *78*, 639. (b) Geoffroy, G. L. *Acc. Chem. Res.* **1980**, *13*, 469. (c) Johnson, B. F. G.; Benfield, R. E. In *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley: Chichester, England, 1980; p 471. (d) Mann, B. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 3, p 89.

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

[3] Some recent examples: (a) Ewing, P.; Farrugia, L. J.; Rycroft, D. S. *Organometallics* **1988**, *7*, 859. (b) Kneuper, H.-J.; Shapley, J. R. *Organometallics* **1987**, *6*, 2455. (c) VanderVelde, D. G.; Holmgren, J. S.; Shapley, J. R. *Inorg. Chem.* **1987**, *26*, 3077. (d) Aime, S.; Bertoncello, R.; Busetti, V.; Gobetto, R.; Granozzi, G.; Osella, D. *Inorg. Chem.* **1986**, *25*, 4004. (e) Hsu, L.-Y.; Hsu, W.-L.; Jan, D.-Y.; Shore, S. G. *Organometallics* **1986**, *5*, 1041.

[4] Willis, A. C.; Einstein, F. W. B.; Ramadan, R. M.; Pomeroy, R. K. *Organometallics* **1983**, *2*, 935.

[5] Broach, R. W.; Williams, J. M. *Inorg. Chem.* **1979**, *18*, 314.

[6] Benfield, R. E.; Johnson, B. F. G.; Lewis, J., Raithby, P. R.; Zuccaro, C.; Henrick, K. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *B35*, 2210.

[7] Aime, S.; Osella, D.; Milone, L.; Rosenberg, E. *J. Organomet. Chem.* **1981**, *213*, 207.

[8] (a) Hawkes, G. E.; Randall, E. W.; Aime, S.; Osella, D.; Elliot, J. E. *J. Chem. Soc., Dalton Trans.* **1984**, 279. (b) Hawkes, G. E.; Lian, L. Y.; Randall, E. W.; Sales, K. D.; Aime, S. *Ibid* **1985**, 225.

[9] Rosenberg, E.; Anslyn, E. V.; Barner-Thorsen, C.; Aime, S.; Osella, D.; Gobetto, R.; Milone, L. *Organometallics* **1984**, *3*, 1790.

[10] Adams, R. D.; Golembeski, N. M. *J. Am. Chem. Soc.* **1979**, *101*, 2579.

[11] Knox, S. A. R.; Koepke, J. W.; Andrews, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 3942.

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

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pounds were obtained from $^{13}$CO-enriched $Os_3(CO)_{12}$ (estimated 35–40% $^{13}$C). This in turn was prepared by heating $Os_3(CO)_{12}$ in toluene at 125 °C under ~1.5 atm of $^{13}$CO (99% $^{13}$C) for 3 days.

Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer; the internal calibration of the instrument was periodically checked against the known absorption frequencies of gaseous CO. The electron-impact (70 eV) mass spectrum was obtained on a Hewlett-Packard 5985 GC–MS system; the pattern of the envelope of peaks of the parent ion matched that simulated by computer. NMR spectra were recorded on a Bruker WM400 or a Bruker SY-100 spectrometer; $^{13}$C NMR spectra were obtained on samples that had been $^{13}$CO enriched. The NMR line-shape simulations were carried out with a computer program written by Professor R. E. D. McClung of the University of Alberta or the program DNMR3 of Kleier and Binch.[13] The microanalysis was performed by M. K. Yang of the Microanalytical Laboratory of Simon Fraser University.

*Caution*! Hydrogen forms explosive mixtures with air.

**Preparation of $Os_3(\mu\text{-}H)_2(CO)_{10}$.** A 200-mL Parr bomb (fitted with a safety disk rated at 3000 psi) was charged with $Os_3(CO)_{12}$ (0.500 g, 0.552 mmol) and hexane (60 mL) and sealed. The vessel was pressurized with $H_2$ (~65 atm) and then released; this procedure was repeated three times. The bomb was pressurized with $H_2$ (80 atm), sealed, and placed in an oil bath at 180 °C for 15 min; the solution was vigorously stirred during this procedure. The bomb was removed from the oil bath and allowed to cool to 0 °C. The pressure was then released, the bomb opened, and the purple solution transferred to a 500-mL round-bottom flask. Unreacted $Os_3(CO)_{12}$ remained in the bomb. The above procedure was repeated until the $Os_3(CO)_{12}$ had been consumed (usually three cycles). The hexane fractions were combined and stored at −15 °C overnight. The purple solution was decanted from a small amount of precipitate of $Os_4(\mu\text{-}H)_4(CO)_{12}$. The solvent from the solution containing crude $Os_3(\mu\text{-}H)_2(CO)_{10}$ was removed on the rotary evaporator. The purple residue was chromatographed on a silica gel column (2.5 × 20 cm) with hexane as the eluant. The purple fraction was collected and the solvent again removed on the rotary evaporator. The residue was recrystallized from toluene/hexane (1:1) to afford $Os_3(\mu\text{-}H)_2(CO)_{10}$ (0.312 g, 0.366 mmol, 60.9%) as air-stable, deep purple crystals. The spectroscopic properties of the compound were in agreement with those in the literature.[11] (Since $Os_3(CO)_{12}$ and $Os_3(\mu\text{-}H)_2(CO)_{10}$ are air-stable, there is no need to work under nitrogen during the isolation of the product.)

**Preparation of the Green Isomer of $Os_3(\mu\text{-}H)_2(CO)_9(CNBu^t)$ (1g).** A test tube with $HOs_3(\mu\text{-}H)(CO)_{10}(CNBu^t)$ (~5 mg) and hexane (5 mL) was refluxed in air until the color changed from yellow to deep green. This took about 30 s. (Further heating causes the color to change from green to red due to the formation of the red isomers of $Os(\mu\text{-}H)_2(CO)_9(CNBu^t)$.) The green solution was transferred to a Schlenk tube and stored at 0 °C. This procedure was repeated several times. The green solutions were combined, concentrated, filtered, and placed in the refrigerator at −15 °C. A mixture of green crystals of the desired product and yellow crystals of the starting material was obtained. The crystals were extracted with hexane in which the product dissolved rapidly but the starting material was almost insoluble. The product obtained from cooling the hexane extract was further recrystallized from hexane to yield pure $Os_3(\mu\text{-}H)_2(CO)_9(CNBu^t)$ (~80% yield based on the amount of $HOs_3(\mu\text{-}H)(CO)_{10}(CNBu^t)$ consumed). The product was also purified by chromatography on Florisil with hexane as the eluant, but the yields were lower: mp 107–108 °C; IR (hexane) $\nu$(CN) 2177.5 (br, m), $\nu$(CO) 2084.5 (m), 2060.5 (s), 2033.5 (vs), 2004 (s), 1994.5 (s), 1984.5 (m), 1965.5 (m), 1935 (vw) cm$^{-1}$; $^1$H NMR ($C_7D_8$, ambient temperature) $\delta$ 0.73, −10.94 (d, $J_{H-H}$ = 1.1 Hz, $J_{Os-H}$ = 47.2 Hz), −11.36 (d, $J_{H-H}$ = 1.1 Hz, $J_{Os-H}$ = 47.2 Hz); $^{13}$C (hydrogen coupled) NMR ($CH_2Cl_2/CD_2Cl_2$, 4/1, −30 °C, CO region) $\delta$ 187.3 (2 C), 185.3 (1 C), 181.9 (2 C), 178.0 (2 C, d, $J_{C-H}$ = 11.6 Hz), 177.4 (2 C, d, $J_{C-H}$ = 11.7 Hz); MS (EI) *m/z* 909 ($M^+$) Anal. Calcd for $C_{14}H_{11}NO_9Os_3$: C, 18.52; H, 1.22; N, 1.54. Found: C, 18.72; H, 1.27; N, 1.33.

The preparation of **1g** may also be satisfactorily carried out by the rapid heating of solutions of $HOs_3(\mu\text{-}H)(CO)_{10}(CNBu^t)$ in a test tube (1.5 × 15 cm) with a simultaneous purge of the solution with nitrogen. However, when this method is used with a larger reaction vessel such as a Schlenk tube, significant amounts of **1r** are formed.

Spectroscopic data for the red isomers of $Os_3(\mu\text{-}H)_2(CO)_9(CNBu^t)$: IR (hexane) $\nu$(CN) 2174.5 (br, m), $\nu$(CO) 2091.5 (s), 2053.5 (vs), 2027.5 (vs), 2012 (vs), 1999 (s), 1984 (s), 1980 (s), 1967.5 (m), 1943.5 (vw) cm$^{-1}$. $^1$H NMR ($CD_2Cl_2$, −70 °C): **1ra**, $\delta$ 1.42, −11.28 (d, $J_{H-H}$ = 1.1 Hz), −12.72 (d, $J_{H-H}$ = 1.1 Hz); **1rb**, 1.52, −11.47 (s); ratio **1ra**:**1rb** = ~10:3. $^{13}C\{^1H\}$ NMR ($C_7D_8$, 34 °C): **1ra**, $\delta$ 185.8 ($J_{C-C}$ = 34.2 Hz), 185.1, 184.0 ($J_{C-C}$ = 35.2 Hz), 183.3, 178.3, 177.1, 176.4, 176.1, 175.0; **1rb**, $\delta$ 184.1 (2 C), 182.8 (1 C), 182.3 (1 C), 179.0 (2 C), 176.9 (2 C), 176.7 (1 C).

**X-ray Structure Determination of 1g.** Crystals of **1g** of acceptable quality were grown from hexane. Diffraction data were collected on an Enraf-Nonius CAD4F diffractometer at 20 ± 1 °C with the use of graphite-monochromated Mo K$\alpha_1$ radiation ($\lambda$ = 0.709 26 Å). Background measurements were made by extending the scan range by 25% on each side of the scan. Accurate cell dimensions were assigned on the basis of 25 accurately centered reflections with $25.0° < 2\theta < 36.0°$. The diffraction data were corrected for Lorentz, polarization, and absorption effects (because the crystal had an irregular shape that could not be adequately modeled an empirical absorption correction was used).[14]

The osmium atoms were located by the Patterson method; the remaining non-hydrogen atoms were located from Fourier difference maps after least-squares refinement. After anisotropic refinement of the osmium, nitrogen, and oxygen atoms, one hydrogen atom of each of the methyl groups was located from a Fourier difference map that employed inner data only. The remaining methyl hydrogen atoms were placed at calculated positions ($d$(C–H) = 0.95 Å). These positions were not refined but were recalculated after refinement of all other atoms. The hydride ligands were not located or included in calculations. Unit weights were used in the initial stages of refinement. After the refinement had converged, the weight, $w$, for each reflection was set to be $w = [\sigma^2(F) + KF^2]^{-1}$ and the value of $K$ adjusted to remove trends in the average $w\Delta^2/\lambda$ as a function of $|F_o|$ and $(\sin \theta)/\lambda$. Two weak, low-angle reflections that had asymmetric backgrounds and the largest $w\Delta^2$ values (an order of magnitude greater than the next largest $w\Delta^2$) were removed from the final cycles of refinement. Final convergence was achieved by full-matrix least-squares refinement. The largest peaks in the final Fourier difference map were in the vicinity of the osmium atoms. Crystallographic data and details of the data collection are given in Table I, atomic coordinates in Table II, and bond length and angle data in Table III. Neutral-atom scattering factors with anomalous dispersion corrections were employed.[15] The computer programs used were from "The NRC VAX 750/780 Crystal Structure System"[16] except that the SNOOPI program[17] was used to draw the atomic thermal ellipsoid diagram.

## Results and Discussion

Rapid heating in air of hexane solutions of $HOs_3(\mu\text{-}H)(CO)_{10}(CNBu^t)$ (**2a,b**) to reflux causes the color to change from yellow to green and then to red. (The rapid heating with the simultaneous outgassing of the solution are essential to observe the formation of the green phase.) The yellow color can be restored by treating either the green or red solutions at room temperature with carbon monoxide. The red color is due to the known isomers of $Os_3(\mu\text{-}H)_2(CO)_9(CNBu^t)$ (**1ra,b**; Scheme I).[10] If the reaction is stopped at the first color change, a green crystalline compound can be isolated, the mass spectrum and chemical analysis of which indicates it also has the formula

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(13) Kleier, D. A.; Binsch, G. *QCPE* **1970**, *11*, 165.

(14) North, A. C. T.; Phillips, D. C.; Mathews, F. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 351.

(15) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1.

(16) Gabe, E. *The NRC Crystal Structure System*; Chemistry Division, National Research Council: Ottawa, 1983.

(17) Davies, E. K. *CHEMGRAF Program Suite*; Chemical Crystallography Laboratory: University of Oxford, Oxford, U.K., 1982.

**Table I. Summary of Crystal Data for $Os_3(\mu\text{-}H)_2(CO)_9(CNBu^t)$ (1g)**

| | |
|---|---|
| formula | $C_{14}H_{11}O_9Os_3N$ |
| fw | 905.6 |
| color | dark green |
| space group | $P2_1/n$[a] |
| cryst sys | monoclinic |
| temp, °C | 23 ± 2 |
| $a$, Å | 11.341 (2) |
| $b$, Å | 12.106 (2) |
| $c$, Å | 16.225 (2) |
| $\beta$, deg | 108.43 (1) |
| $V$, Å$^3$ | 2113.3 |
| $Z$ | 4 |
| $d$(calcd), g cm$^{-3}$ | 2.853 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 180.6 |
| cryst size, mm | 0.15 × 0.15 × 0.06 |
| scan method | $\omega$–2$\theta$ |
| 2$\theta$ range, deg | 2.5–50.0 |
| scan width (2$\theta$), deg | 0.85 ± 0.35 tan $\theta$ |
| scan rate (2$\theta$), deg min$^{-1}$ | 0.92–2.75 |
| collcn range | $+h,+k,\pm l$ |
| transmission coeff range[b] | 0.39–1.00 |
| no. of unique data | 3701 |
| no. of observed data ($I \geq 2.5\sigma(I)$) | 2044 |
| no. of variables | 189 |
| $R_1$[c] | 0.034 |
| $R_2$[d] | 0.034 |
| $K$ factor in wt scheme[e] | 0.0002 |
| GOF | 1.140 |
| largest shift/error[f] | 0.07 |
| largest peak,[g] e Å$^{-3}$ | 1.1 (2) |

[a] Nonstandard setting of $P2_1/c$. [b] Normalized transmission factors. [c] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum|wF_o|^2]^{1/2}$. [e] See text. [f] Largest shift/error in final cycle of refinement. [g] Largest peak and standard deviation in final Fourier difference map.

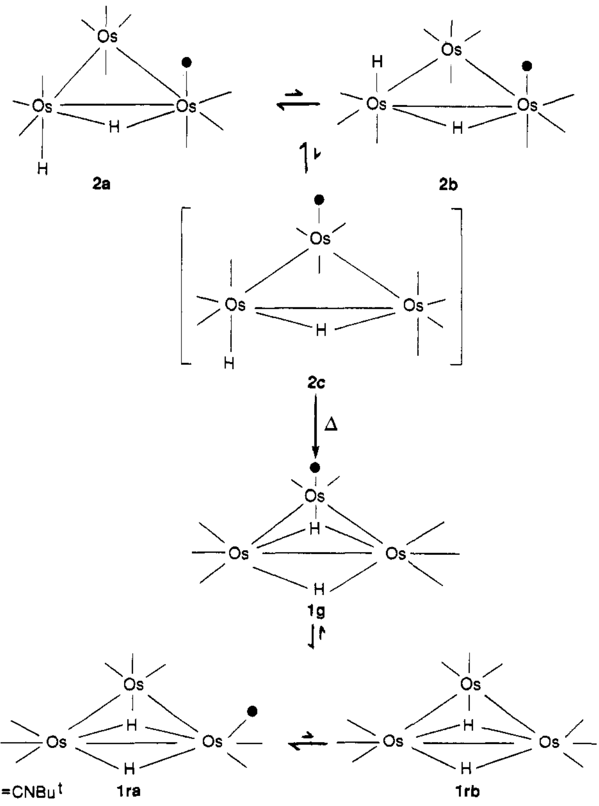
**Table II. Fractional Coordinates for 1g**

| atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Os(1) | 0.29983 (6) | 0.14808 (5) | 0.01444 (4) |
| Os(2) | 0.26828 (6) | 0.37699 (5) | 0.02823 (4) |
| Os(3) | 0.09315 (6) | 0.26420 (6) | −0.09238 (4) |
| N | 0.4219 (12) | 0.2010 (11) | −0.1313 (8) |
| O(11) | 0.2445 (17) | −0.0861 (12) | −0.0551 (9) |
| O(12) | 0.5492 (13) | 0.1081 (12) | 0.1532 (8) |
| O(13) | 0.1487 (12) | 0.1332 (11) | 0.1415 (7) |
| O(21) | 0.1910 (12) | 0.6205 (11) | 0.0014 (8) |
| O(22) | 0.3221 (13) | 0.3781 (11) | 0.2232 (6) |
| O(23) | 0.5434 (11) | 0.3891 (10) | 0.0505 (7) |
| O(31) | −0.1025 (14) | 0.4258 (12) | −0.1930 (8) |
| O(32) | −0.0907 (13) | 0.0977 (13) | −0.0655 (8) |
| O(33) | 0.1146 (12) | 0.1311 (12) | −0.2451 (7) |
| C(1) | 0.3785 (15) | 0.1808 (13) | −0.0771 (9) |
| C(4) | 0.4715 (16) | 0.2375 (15) | −0.1984 (10) |
| C(5) | 0.3994 (26) | 0.1783 (23) | −0.2826 (11) |
| C(6) | 0.6061 (25) | 0.1970 (22) | −0.1709 (14) |
| C(7) | 0.4618 (30) | 0.3583 (20) | −0.2091 (15) |
| C(11) | 0.2629 (17) | 0.0038 (16) | −0.0298 (11) |
| C(12) | 0.4588 (19) | 0.1231 (16) | 0.1020 (12) |
| C(13) | 0.2035 (16) | 0.1373 (14) | 0.0955 (10) |
| C(21) | 0.2198 (17) | 0.5275 (16) | 0.0120 (10) |
| C(22) | 0.3052 (14) | 0.3791 (13) | 0.1506 (9) |
| C(23) | 0.4388 (17) | 0.3878 (14) | 0.0439 (10) |
| C(31) | −0.0271 (17) | 0.3658 (15) | −0.1518 (11) |
| C(32) | −0.0204 (17) | 0.1609 (15) | −0.0771 (10) |
| C(33) | 0.1046 (17) | 0.1794 (15) | −0.1877 (11) |

**Table III. Selected Molecular Dimensions for $Os_3(\mu\text{-}H)_2(CO)_9(CNBu^t)$**

| | | | |
|---|---|---|---|
| Bond Lengths (Å) | | | |
| Os(1)–Os(2) | 2.812 (1) | C(1)–N | 1.16 (2) |
| Os(1)–Os(3) | 2.812 (1) | C(11)–O(11) | 1.16 (2) |
| Os(2)–Os(3) | 2.680 (1) | C(12)–O(12) | 1.11 (2) |
| Os(1)–C(1) | 2.00 (2) | C(13)–O(13) | 1.12 (2) |
| Os(1)–C(11) | 1.88 (2) | C(21)–O(21) | 1.17 (2) |
| Os(1)–C(12) | 1.93 (2) | C(22)–O(22) | 1.13 (2) |
| Os(1)–C(13) | 1.96 (2) | C(23)–O(23) | 1.16 (2) |
| Os(2)–C(21) | 1.90 (2) | C(31)–O(31) | 1.16 (2) |
| Os(2)–C(22) | 1.90 (2) | C(32)–O(32) | 1.16 (2) |
| Os(2)–C(23) | 1.87 (2) | C(33)–O(33) | 1.14 (2) |
| Os(3)–C(31) | 1.86 (2) | N–C(4) | 1.44 (2) |
| Os(3)–C(32) | 1.87 (2) | C(4)–C(5) | 1.53 (3) |
| Os(3)–C(33) | 1.90 (2) | C(4)–C(6) | 1.53 (3) |
| | | C(4)–C(7) | 1.47 (3) |
| Bond Angles (deg) | | | |
| Os(1)–Os(2)–Os(3) | 61.53 (3) | N–C(1)–Os(1) | 179 (2) |
| Os(2)–Os(3)–Os(1) | 61.55 (3) | O(11)–C(11)–Os(1) | 177 (2) |
| Os(3)–Os(1)–Os(2) | 56.91 (2) | O(12)–C(12)–Os(1) | 179 (2) |
| C(1)–Os(1)–Os(3) | 85.6 (5) | O(13)–C(13)–Os(1) | 179 (2) |
| C(1)–Os(1)–C(11) | 89.9 (7) | O(21)–C(21)–Os(2) | 179 (2) |
| C(1)–Os(1)–C(12) | 92.6 (7) | O(22)–C(22)–Os(2) | 177 (2) |
| C(1)–Os(1)–C(13) | 170.1 (7) | O(23)–C(23)–Os(2) | 176 (2) |
| C(11)–Os(1)–C(12) | 100.2 (8) | O(31)–C(31)–Os(3) | 176 (2) |
| C(21)–Os(2)–C(22) | 95.2 (8) | O(32)–C(32)–Os(3) | 178 (2) |
| C(21)–Os(2)–C(23) | 101.2 (8) | O(33)–C(33)–Os(3) | 177 (2) |
| C(22)–Os(2)–C(23) | 88.9 (7) | C(5)–C(4)–N | 108 (2) |
| C(23)–Os(2)–Os(3) | 129.0 (5) | C(6)–C(4)–N | 106 (2) |
| C(31)–Os(3)–C(32) | 95.1 (8) | C(7)–C(4)–N | 111 (2) |
| C(31)–Os(3)–C(33) | 99.4 (8) | C(1)–N–C(4) | 174 (2) |
| C(32)–Os(3)–C(33) | 88.5 (8) | C(5)–C(4)–C(6) | 108 (2) |
| C(33)–Os(3)–Os(2) | 130.2 (6) | C(5)–C(4)–C(7) | 111 (2) |
| | | C(6)–C(4)–C(7) | 113 (2) |

**Scheme I**



$Os_3(\mu\text{-}H)_2(CO)_9(CNBu^t)$ (**1g**). The $^1H$ NMR spectrum of **1g** in toluene-$d_8$ at room temperature shows two hydride resonances at $\delta$ −10.94 and −11.36. Although this region is normally associated with terminal hydrides on osmium clusters, it is known that the resonances of the formally unsaturated $Os(\mu\text{-}H)_2Os$ unit also appear in this region.[18]

The isomers of **1r** are known to have the CNBu$^t$ ligand in either a pseudoaxial site (**1ra**) or an equatorial site (**1rb**) of one of the osmium atoms of the $Os(\mu\text{-}H)_2Os$ grouping (Scheme I).[10,19] The most reasonable structure for **1g** was

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[18] Humphries, A. P.; Kaesz, H. D. *Prog. Inorg. Chem.* **1979**, *25*, 145.

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

therefore one with an $Os(\mu\text{-}H)_2Os$ linkage, but with the $CNBu^t$ ligand in an axial site on the osmium atom not associated with this linkage. This structure was confirmed by an X-ray crystallographic study which is reported below.

When a solution of **1g** in $CH_2Cl_2$ was stirred at room temperature, it isomerized over 4 days to give an equilibrium mixture of **1ra**, **1rb**, and **1g** in an approximate ratio of 5:1:1 (by $^1H$ NMR spectroscopy). This, of course, indicates **1g** is the kinetic product from the decarbonylation of **2** and is an apparent example of a kinetically favored dissociation of CO from one metal center in a trinuclear metal carbonyl cluster. That **1g** is formed rather than **1r** is surprising given the structures of **2a** and **2b** (Scheme I). It suggests that the decarbonylation may proceed through an intermediate such as **2c** (or the isomer similar to **2c** but with the $CNBu^t$ ligand on the same side of the $Os_3$ plane as the terminal hydride ligand). In **2c** the bridging hydride could labilize a CO group of the $Os(CO)_4$ unit to facilitate the formation of the second bridging hydride. This may not occur in **2a** or **2b** since the Os–C bonds to the carbonyls of $Os(CO)_3(CNBu^t)$ are expected to be stronger than those in $Os(CO)_4$ because of the presence of the $CNBu^t$ ligand with its weaker $\pi$-acceptor, stronger $\sigma$-donor properties than those of CO. A closer investigation of the $^1H$ NMR spectrum of **2** in $CD_2Cl_2$ at −70 °C revealed three, weak signals at $\delta$ 1.67, −8.57, and −19.46 that had not been previously reported and which could indicate the presence of a third isomer of **2** such as **2c**.

If **2c** is involved in the formation of **1g**, it probably arises from the migration of the bridging hydride ligand in **2a** from one edge of the $Os_3$ triangle to another. Such processes are known to have low activation barriers in hydridoosmium clusters.[2,3] Other mechanisms such as simultaneous CO–$CNBu^t$ exchange cannot, however, be ruled out.

Also of interest are the small couplings (~1 Hz) between the chemically different protons in the $^1H$ NMR spectra of both **1g** and **1ra**. The bonding of the $Os(\mu\text{-}H)_2Os$ fragment in the parent $Os_3(\mu\text{-}H)_2(CO)_{10}$ has been described in terms of four-center, four-electron bonds.[5,20] The small coupling between the hydrides in **1g**, and in **1ra**, suggests that in these complexes there is little mixing of the molecular orbitals of each $Os(\mu\text{-}H)Os$ unit of the $Os(\mu\text{-}H)_2Os$ grouping.[21] We have observed similar couplings for the $Os(\mu\text{-}H)_2Os$ unit of $Os_3(\mu\text{-}H)_3(CO)_9(SiPh_3)$.[4] The $^1H$ NMR signals of **1g** exhibited detectable couplings to $^{187}Os$ (1.6% natural abundance) of 47.2 Hz. These couplings are consistent with our previous observation that $^{187}Os$ coupling to hydrides of $Os(\mu\text{-}H)_2Os$ linkages are greater than ~40 Hz whereas the corresponding coupling to hydrides of $Os(\mu\text{-}H)Os$ units are less than ~40 Hz.[4]

**Structure of 1g.** A view of the molecule is shown in Figure 1; bond lengths and angles are given in Table III. Although the hydride ligands were not located, they almost certainly both bridge Os(2)–Os(3). The short distance for the Os(2)–Os(3) vector (2.680 (1) Å) is characteristic of the $Os(\mu\text{-}H)_2Os$ unit. For example, in **1rb** the corresponding distance is 2.690 (1) Å;[19] in $Os_3(\mu\text{-}H)_2(CO)_{10}$ it is 2.683 (1) Å.[5] (The latter distance was determined by a neutron diffraction study in which the bridging hydrides were accurately located.) The other Os–Os vectors in **1g** (both are 2.812 (1) Å) are somewhat shorter than normally found in trinuclear osmium carbonyl clusters (in $Os_3(CO)_{12}$, for example, the average Os–Os bond length is 2.877 (3) Å[22]). A similar shortening of unbridged Os–Os bonds in triosmium clusters with the $Os(\mu\text{-}H)_2Os$ group is observed in **1rb**[19] and $Os_3(\mu\text{-}H)_2(CO)_9(L)$ (L = CO,[5] $PPh_3$[6]).

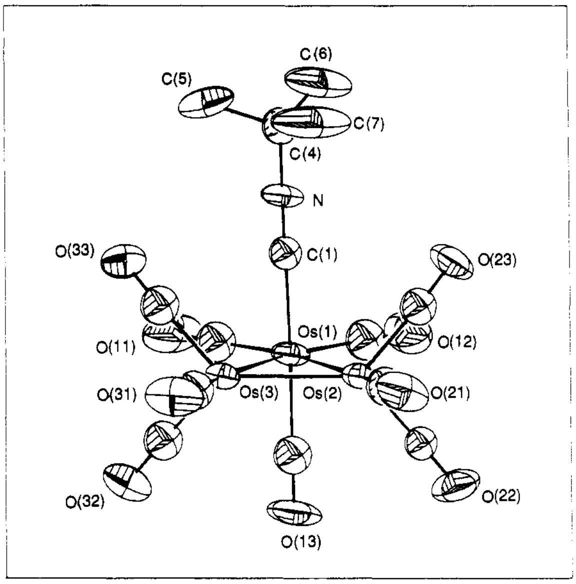
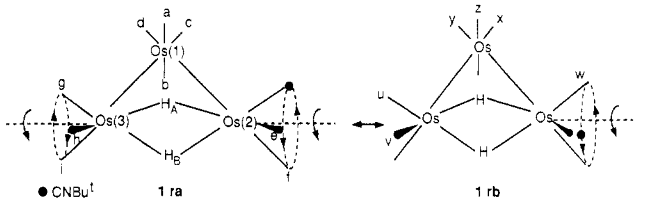


**Figure 1.** Molecular structure of $Os_3(\mu\text{-}H)_2(CO)_9(CNBu^t)$ (**1g**).

**Scheme II**



In contrast to **1rb**,[19] the isocyanide ligand is bound to the osmium atom not associated with the $Os(\mu\text{-}H)_2Os$ unit and occupies an axial site. It has been observed previously that whereas bulky ligands such as phosphines occupy equatorial positions in trinuclear clusters,[23,24] sterically less demanding ligands such as isocyanide[19,25,26] and terminal hydride ligands[19,22,24] usually (but not always[19,27]) adopt axial sites. The Os–C bond length to the isocyanide group is marginally longer than the corresponding length to the axial carbonyl on the same osmium atom (2.00 (2) Å vs 1.96 (2) Å). Although the difference is not significant statis-

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[20] Sherwood, D. E.; Hall, M. B. *Inorg. Chem.* **1982**, *21*, 3458. See also: (a) Granozzi, G.; Benoni, R.; Tondello, E.; Casarin, M.; Aime, S.; Osella, D. *Inorg. Chem.* **1983**, *22*, 3899. (b) Green, J. C.; Mingos, D. M. P.; Seddon, E. A. *Inorg. Chem.* **1981**, *20*, 2595.

[21] A reviewer has, however, suggested that the coupling between two hydrogen atoms in a four-center, four-electron bond may still have an angular dependence. The H–Os–H angles were estimated to be ~82°, and the dihedral angle between the Os(1)–$H_A$–Os(2) and Os(1)–$H_B$–Os(2) planes was ~155°. (The positions of the hydride ligands were calculated with the HYDEX program: Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2509.)

[22] Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.

[23] For example: (a) Dahm, D. J.; Jacobson, R. A. *J. Am. Chem. Soc.* **1968**, *90*, 5106. (b) Johnson, B. F. G.; Lewis, J.; Reichert, B. E.; Schorpp, K. T. *J. Chem. Soc., Dalton Trans.* **1976**, 1403. (c) Benfield, R. E.; Johnson, B. F. G.; Raithby, P. R.; Sheldrick, G. M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 666. (d) Bruce, M. I.; Matisons, J. G.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans* **1983**, 2375. (e) Venäläinen, T.; Pakkanen, T. A. *J. Organomet. Chem.* **1984**, *266*, 269. (f) Alex, R. F.; Einstein, F. W. B.; Jones, R. H.; Pomeroy, R. K. *Inorg. Chem.* **1987**, *26*, 3175. (g) Bruce, M. I.; Liddel, M. J.; Hughes, C. A.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1988**, *347*, 157.

[24] Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 2397.

[25] Mays, M. J.; Gavens, P. D. *J. Chem. Soc., Dalton Trans.* **1980**, 911.

[26] Bruce, M. I.; Matisons, J. G.; Wallis, R. C.; Patrick, J. M.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1983**, 2365.

[27] Einstein, F. W. B.; Pomeroy, R. K.; Willis, A. C. *J. Organomet. Chem.* **1986**, *311*, 257.

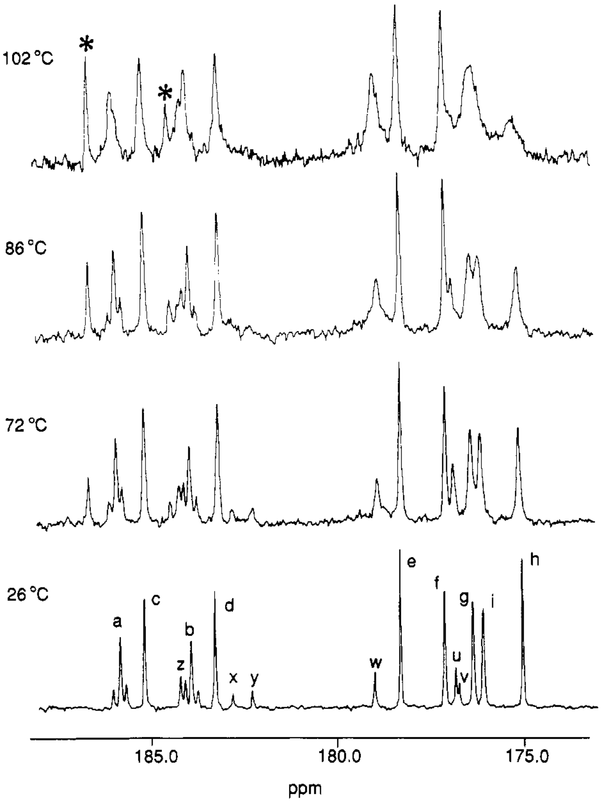

**Figure 2.** Variable-temperature $^{13}C$ NMR spectra of $^{13}CO$-enriched **1r** in toluene/toluene-$d_8$. See Scheme II for the assignment of signals. The peaks marked with an asterisk are due to **1g** that forms at higher temperatures.

tically, it is consistent with the view that CO is usually a better $\pi$-acceptor than the $CNBu^t$ ligand.[28] A similar lengthening of the Os–C($CNBu^t$) bond distance compared to the Os–C($CO_{eq}$) is observed in **1rb**.[19]

**Nonrigidity in 1r.** In solution, **1r** consists of two isomers, the major isomer (**1ra**) has the $CNBu^t$ ligand in a pseudoaxial site of an osmium atom of the $Os(\mu\text{-}H)_2Os$ unit; the minor isomer (**1rb**) is similar except that the isocyanide ligand is in an equatorial site (see Schemes I and II).[10] (In the solid state **1r** exists as isomer **b**.[19])

The $^{13}C\{^1H\}$ NMR spectrum of **1r** in $CD_2Cl_2/CH_2Cl_2$ at room temperature (Figure 2) is consistent with the view that **1ra** is the major isomer in solution: there are nine major signals in the spectrum at $\delta$ 185.8, 185.1, 184.0, 183.3, 178.3, 177.1, 176.4, 176.1, and 175.0. The signals at 185.8 and 184.0 ppm may be readily assigned to the axial carbonyls a and b (Scheme II) since they are the only signals that exhibit $^{13}C$–$^{13}C$ coupling as expected for a trans OC–Os–CO arrangement.[29]

It is well-known that C≡N triple bonds possess particularly strong magnetic anisotropies, and it has been found that in regions alongside the triple bond deshielding occurs.[30] With one exception it is found that, in those cases where assignment is unambiguous, the NMR resonances of the hydride and carbonyl ligands nearest to the $CNBu^t$ ligand in both **1r** and **1g** are shifted downfield. In cases where a choice of assignments exists, we therefore assigned the resonance further downfield as due to the carbonyl closest to the $CNBu^t$ ligand. This method of assignment does, however, have limitations. The magnetic anisotropy of CO[31] (and perhaps the $Os(\mu\text{-}H)_2Os$ unit) is also expected to be large. These anisotropies also have angular dependencies so that it is not clear which regions are shielded or deshielded. As we have mentioned, there is one known exception to this method that is described below. With these limitations in mind we tentatively assign the signal at $\delta$ 185.8 to carbonyl a and that at $\delta$ 184.0 to carbonyl b. From the selective hydrogen coupling experiments and the mode of collapse of the signals, discussed below, the two other resonances to low field of 180 ppm (i.e., those at 185.1 and 183.3 ppm) are assigned to the equatorial carbonyls c and d of the $Os(CO)_4$ unit, respectively.

The five major signals to high field of 180 ppm in the spectrum of **1r** can be unambiguously assigned. When the $^1H$ NMR signal at −11.3 ppm is decoupled, only one resonance in the $^{13}C$ NMR spectrum (at $\delta$ 176.4) shows C–H coupling. The latter signal may therefore be assigned to carbonyl g and the proton resonance at −12.7 ppm to $H_B$ since this proton has only one carbonyl (carbonyl g) in a trans position to it. The $^1H$ NMR signal at −11.3 ppm may be assigned to $H_A$ (note it is nearest to the $CNBu^t$ group and its resonance is further downfield than that due to $H_B$). Decoupling $H_B$ results in the expected splitting of two of the signals (at $\delta$ 177.1 and 176.1) in the $^{13}C$ NMR spectrum due to coupling to $H_A$. From the pattern of collapse of the signals (discussed below) the signal at $\delta$ 177.1 may be assigned to carbonyl f and that at $\delta$ 176.1 to carbonyl i. Once again, the downfield signal is due to the carbonyl closest to the $CNBu^t$ ligand. By similar reasoning, the signal at $\delta$ 178.3 may be attributed to carbonyl e and that at $\delta$ 175.0 to carbonyl h. The complete assignment of the signals is shown in Figure 2 and Scheme II.

The assignment of the signals due to the minor isomer **1rb**, shown in Scheme II and Figure 2, followed similar lines although intensity considerations made selective hydrogen-decoupling experiments unnecessary. The hydrogen-coupled spectrum was, however, consistent with the assignments shown.

The assignment of the resonances of the axial and equatorial carbonyls of the $Os(CO)_4$ group of $Os_3(\mu\text{-}H)_2(CO)_{10}$ (**3**) is presently uncertain.[8] A comparison of the spectrum of **3** with that of **1ra** suggests that the low-field resonance at $\delta$ 182.7 in the spectrum of **3** should be assigned to the axial carbonyls and the resonance at $\delta$ 181.8 to the equatorial carbonyls.

On warming the solution of **1r** to 72 °C the $^{13}C$ NMR signals attributed to carbonyls g, h, and i broaden whereas the signals due to the other carbonyls remain sharp (Figure 2). This is consistent with a localized 3-fold exchange of the carbonyls of the $Os(CO)_3$ unit of **1ra** as shown in Scheme II. Simulation of the spectrum at 86 ± 2 °C (Figure 3) gave a rate of 12 ± 2 $s^{-1}$ which corresponds to a $\Delta G^{\ddagger} = 19.4 \pm 0.2$ kcal $mol^{-1}$ for the process. As discussed below, a similar exchange, but with a lower activation barrier, is observed in **1g**. This type of exchange was also found for $Os_3(\mu\text{-}H)_2(CO)_{10}$.[7,8]

At slightly higher temperatures the signals assigned to carbonyls e and f also began to broaden and collapse. Coincidental with this collapse was a general collapse of the resonances of the $Os(CO)_4$ unit of **1ra** and those due to the minor isomer **1rb** (Figure 2). This behavior is consistent with a 3-fold rotation of the ligands of the $Os(CO)_2(CNBu^t)$ unit (i.e., Os(2)); as shown in Scheme II this interconverts isomers **1ra** and **1rb**.

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[28] (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; p 62. (b) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon: New York, 1984; p 349.

[29] (a) Tachikawa, M.; Richter, S. I.; Shapley, J. R. *J. Organomet. Chem.* **1977**, *128*, C9. (b) Aime, S.; Osella, D. *J. Chem. Soc., Chem. Commun.* **1981**, 300.

[30] Günther, H. *NMR Spectroscopy*; Wiley: New York, 1980; p 73.

[31] Gleeson, J. W.; Vaughan, R. W. *J. Chem. Phys.* **1983**, *78*, 5384.

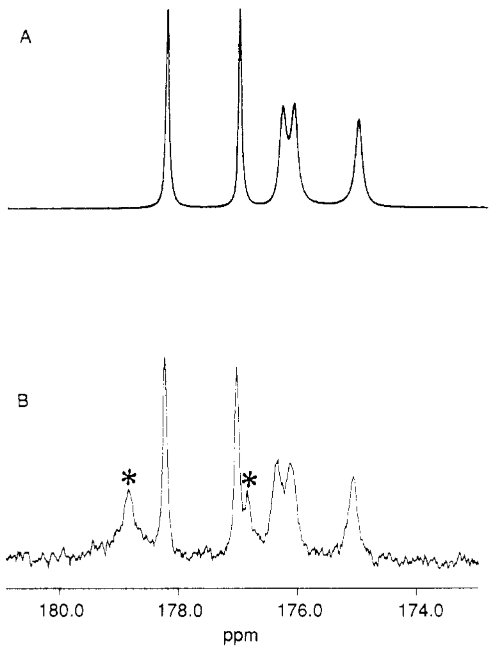
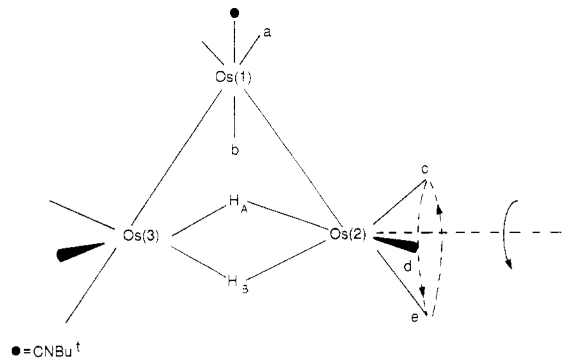


**Figure 3.** Calculated (A) and observed (B) $^{13}C$ NMR spectra (from δ 173 to δ 181) of **1r** in toluene/toluene-$d_8$ at 86 °C (100.6-MHz operating frequency). The peaks marked with an asterisk in B are due to **1rb** and are not included in A.

**Chart I**



The 400-MHz $^1H$ NMR spectrum of **1r** in toluene-$d_8$ at room temperature has two signals in the ratio of ~10:3 at δ 1.42 and 1.52 assigned to the resonances of the *tert*-butyl groups of **1ra** and **1rb**, respectively. On warming to 83 °C these two signals coalesced in agreement with rapid interconvertion of the isomers as depicted in Scheme II. Simulation of the spectrum at 83 ± 2 °C gave a rate of 4.4 ± 0.4 $s^{-1}$ and hence $\Delta G^{\ddagger} = 19.9 \pm 0.2$ kcal mol$^{-1}$ for the isomerization. The hydride signals due to **1ra** and **1rb** had also broadened at this temperature consistent with the isomerization process. Surprisingly, the hydride ligands are rigid on the NMR time scale up to the point of isomerization. Indeed, the hydrides may remain rigid during the isomerization, but there is no simple way of ascertaining this.

**Nonrigidity in 1g.** The $^{13}C\{^1H\}$ NMR spectrum of **1g** in $CD_2Cl_2/CH_2Cl_2$ at -42 °C exhibits five signals at δ 187.3, 185.3, 181.9, 178.0, and 177.4 in an approximate ratio of 2:1:2:2:2 (Figure 4). In the hydrogen-coupled spectrum the two highest field signals (i.e., at δ 178.0 and 177.4) were split into doublets with couplings of 11.6 and 11.7 Hz, respectively. (The couplings are similar to the corresponding coupling found in $Os_3(\mu\text{-}H)_2(CO)_{10}$.[7]) These signals may therefore be assigned to carbonyls c and e (Chart I). We are, however, unable to distinguish further the resonances due to these carbonyls. It was anticipated that because of the proximity of $H_A$ and carbonyl c to the CNBu$^t$ group that the $^1H$ NMR resonance of $H_A$ and the $^{13}C$ NMR resonance of carbonyl c would both be to lower field than the corresponding signals due to $H_B$ and carbonyl e. Because only trans H–C couplings are significant, decoupling $H_A$ will cause collapse of the doublet due to carbonyl e which, as stated, was expected to be at higher field to the doublet attributed to carbonyl c. However, when the $^1H$ NMR resonance at lower field (at δ -10.94) was selectively decoupled, the doublet in the $^{13}C$ NMR spectrum to lower field (at δ 178.0) collapsed to a singlet. Likewise, when the $^1H$ NMR resonance at δ -11.36 was selectively decoupled, the doublet at δ 177.4 in the $^{13}C$ NMR spectrum collapsed to a singlet. This indicates that the original assumption was incorrect. An unambiguous assignment of the hydride resonances, and the resonances due to carbonyls c and e, is therefore presently not possible. One set of resonances must be an exception to the observation that groups nearest the CNBu$^t$ ligand give rise to the NMR signal to lower field.

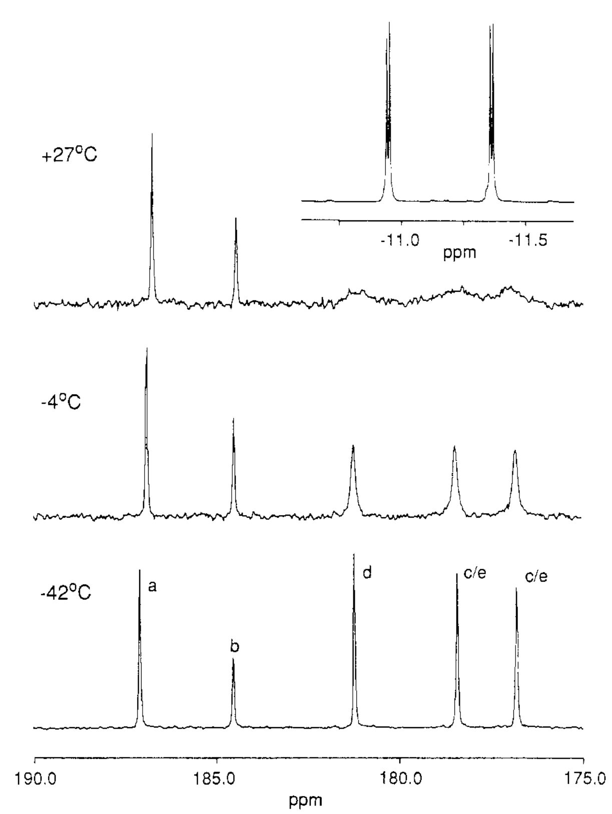


**Figure 4.** Variable-temperature $^{13}C$ NMR spectra of $^{13}CO$-enriched **1g** in $CH_2Cl_2/CD_2Cl_2$ (100.6-MHz operating frequency). The assignment of the signals is as shown in Chart I. Inset: 100-MHz $^1H$ spectrum of **1g** in toluene-$d_8$ at 22 °C.

In a further attempt to assign the hydride resonances an NOE experiment was carried out. Irradiation of the $^1H$ NMR resonance of either hydride signal caused no enhancement to the corresponding resonance of the methyl protons of the isocyanide ligand and vice versa. The experiment probably failed because the closest approach of the hydrogen atoms of the methyl groups to $H_A$ is calculated to be close to the limit at which a nuclear Overhauser effect is expected to be observed[32,33] (the calculated distance is approximately 2.9 Å). Furthermore, the system is a pseudo, three-spin system (methyl proton, $H_A$, $H_B$), and it is relative disposition of all interacting spins that

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[32] Noggle, J. H.; Schirmer, R. E. *The Nuclear Overhauser Effect*; Academic: New York, 1971.

[33] Bell, R. A.; Saunders, J. K. *Can. J. Chem.* **1970**, *48*, 1114.

determine the nuclear Overhauser enhancement rather than simply the distance between the irradiated and observed spin.[32] For this reason the enhancement may be less than that expected for a two-spin system.[32] When one hydride resonance was irradiated, a large nuclear Overhauser enhancement was observed to the other hydride resonance, as expected from the short distance between $H_A$ and $H_B$. It was the study[34] of the nuclear Overhauser effects in hydridoosmium clusters that initially prompted our synthesis of **1r**.

From the mode of collapse of the signals in the $^{13}C$ NMR spectrum of **1g** at higher temperature (discussed below) the signal at $\delta$ 181.9 is attributed to the equatorial carbonyls on the osmium atoms of the $Os(\mu\text{-}H)_2Os$ unit (i.e., the carbonyls labeled d in Chart I). Consistent with this assignment is that in the hydrogen-coupled $^{13}C$ NMR spectrum this signal was broadened due to unresolved cis H–C couplings (the signals at $\delta$ 187.3 and 185.3 were unaffected). The remaining signals may be unambiguously assigned on the basis of intensities: the signal of intensity 1, at $\delta$ 185.3, is assigned to the carbonyl trans to the $CNBu^t$ ligand (i.e., carbonyl b) and that of intensity 2, at $\delta$ 187.3, to the equatorial carbonyls of the $Os(CO)_3(CNBu^t)$ unit (i.e., carbonyls a). That the resonances due to the equatorial carbonyls come to lower field than that due to the axial carbonyl is unusual since in most (saturated) osmium clusters the $^{13}C$ NMR resonances of the equatorial carbonyls come to higher field of the resonances of the axial carbonyls (attached to the same osmium atom).[7,25,35] The anomaly in **1g** is undoubtedly due to the magnetic anisotropy of the $CNBu^t$ and $Os(\mu\text{-}H)_2Os$ units; as mentioned above, the chemical shifts of the hydride ligands of $Os(\mu\text{-}H)_2Os$ units are also anomalous.

On warming the solution of **1g** the signals associated with carbonyls c, d, and e broadened and collapsed to the base line such that at room temperature these signals could not be observed (Figure 4). The peaks due to the carbonyls of the $Os(CO)_3(CNBu^t)$ unit remained sharp to ~70 °C at which temperature conversion to **1r** and consequent loss of signal intensity occurred. This behavior is consistent with a localized 3-fold carbonyl exchange at the osmium atoms of the $Os(\mu\text{-}H)_2Os$ unit (i.e., Os(2) and Os(3)) as shown in Chart I and similar to those proposed for **1ra** and **1rb**.[36]

Simulation of the $^{13}C$ NMR spectrum of **1g** at 8 ± 2 °C yielded a rate constant of $40 \pm 4\ s^{-1}$ and hence a $\Delta G^{\ddagger} = 14.4 \pm 0.2$ kcal $mol^{-1}$. The barrier is significantly lower than that for the corresponding process for the $Os(CO)_3$ unit in **1ra** ($\Delta G^{\ddagger} = 19.4$ kcal $mol^{-1}$) and $Os_3(\mu\text{-}H)_2(CO)_{10}$ ($\Delta G^{\ddagger} = 17.5$ kcal $mol^{-1}$).[38] The difference can be attributed to electronic rather than steric factors.

There is the surprising result that during the carbonyl exchange in **1g** the hydride ligands remain rigid as evidenced by the sharp $^1H$ NMR resonances obtained for the compound at room temperature (Figure 4) and, indeed, at 70 °C. This observation supports the proposal, mentioned in the Introduction, that the hydride ligands in $Os_3(\mu\text{-}H)_2(CO)_{10}$ are rigid during the exchange of the carbonyls bound to the osmium atoms of the $Os(\mu\text{-}H)_2Os$ linkage.[9] The rigidity of the $Os(\mu\text{-}H)_2Os$ unit in **1r** and **1g** may be contrasted to the behavior of hydrides in $Os(\mu\text{-}H)Os$ linkages that usually exhibit nonrigidity when it can be detected.[2,3] In $Os_3(\mu\text{-}H)_3(CO)_9(SiPh_3)$ (4), a molecule with both $Os(\mu\text{-}H)Os$ and $Os(\mu\text{-}H)_2Os$ units, the different protons of the $Os(\mu\text{-}H)_2Os$ undergo exchange at a detectable rate above ~50 °C.[4] Although not studied in detail some of the carbonyls in 4 also undergo exchange at this temperature. In clusters of the type $HOs_3(\mu\text{-}H)(CO)_{10}(L)$, which are derived from $Os_3(\mu\text{-}H)_2(CO)_{10}$, there is rapid exchange of the terminal and bridging hydrides.[7,12] The nonrigidity of the carbonyls in the isomers of 1 may be contrasted with that in clusters of the type $Os_3(\mu\text{-}H)(\mu\text{-}X)(CO)_{10}$ (X = SEt, SPh, Cl, Br, I, $CO_2Me$, $CO_2CF_3$) where there is carbonyl exchange in the $Os(CO)_4$ rather than the $Os(CO)_3$ units.[39] In $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$, which contains both $Re(\mu\text{-}H)Re$ and $Re(\mu\text{-}H)_2Re$ linkages, the two types of hydrides do not exchange nor do the carbonyls of the $Re(CO)_3$ and $Re(CO)_4$ groups.[40] Thus, although recent work by several groups have clearly demonstrated the types of nonrigid processes that can occur in metal carbonyl clusters, it is not clear why some of these processes have low activation barriers whereas other similar processes do not.

**Acknowledgment**. We thank the Natural Sciences and Engineering Research Council for financial support.

**Registry No.** **1g**, 123813-04-7; **1ra**, 123878-75-1; **1rb**, 123878-76-2; **2a**, 69942-19-4; **2b**, 123878-74-0; **2c**, 123813-03-6; $Os_3(\mu\text{-}H)_2(CO)_{10}$, 41766-80-7; $Os_3(CO)_{12}$, 15696-40-9; $Os_4(\mu\text{-}H)_4(CO)_{12}$, 12375-04-1.

**Supplementary Material Available:** Tables of hydrogen atom coordinates and thermal parameters for **1g** (2 pages); a listing of observed and calculated structure factors for **1g** (15 pages). Ordering information is given on any current masthead page.

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[34] (a) Ma, A. K.; Pomeroy, R. K., to be submitted for publication. (b) Ma, A. K.; Pomeroy, R. K. *Abstracts of Papers*; Third Chemical Congress of North America, Toronto; American Chemical Society: Washington, D.C., 1988; IN393.

[35] (a) Mann, B. E.; Taylor, B. F. *$^{13}C$ NMR Data for Organometallic Compounds*; Academic: New York, 1981; p 176 and references therein. (b) Alex, R. F.; Pomeroy, R. K. *Organometallics* **1987**, *6*, 2437.

[36] We have suggested that some fluxional processes in metal clusters may involve a metal atom rotating with its attached ligands.[37] There is, however, no way of distinguishing by NMR techniques whether the osmium atoms are rigid or not in the nonrigid processes exhibited by the isomers of 1.

[37] Davis, H. B.; Einstein, F. W. B.; Johnston, V. J.; Pomeroy, R. K. *J. Am. Chem. Soc.* **1988**, *110*, 4451.

[38] Calculated from data given in ref 8.

[39] Bryan, E. G.; Forster, A.; Johnson, B. F. G.; Lewis, J.; Matheson, T. W. *J. Chem. Soc., Dalton Trans.* **1978**, 196.

[40] Beringhelli, T.; Ciani, G.; D'Alphonso, G.; Molinari, H.; Sironi, A. *Inorg. Chem.* **1985**, *24*, 2666.