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# THE SYNTHESIS, CRYSTAL AND MOLECULAR STRUCTURE OF *syn*-$HOs_3[\mu\text{-}\eta^1\text{-}N{=}C(H)CF_3](CO)_9PMe_2Ph$

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## Summary

The compound *syn*-$HOs_3[\mu\text{-}\eta^1\text{-}N{=}C(H)CF_3](CO)_9PMe_2Ph$ is one of two isomers which have been obtained from the reaction of $HOs_3[\mu\text{-}\eta^1\text{-}N{=}C(H)CF_3](CO)_{10}$ with the $PMe_2Ph$. It has been characterized by X-ray crystallographic methods and $^1H$ NMR spectroscopy. It crystallizes in the space group $P\bar{1}$, $a$ = 9.067(2) Å, $b$ = 9.436(2) Å, $c$ = 15.994(2) Å; $\alpha$ = 102.25(2), $\beta$ = 94.41(2), $\gamma$ = 92.26(2)°; $V$ = 1331.1(13) Å$^3$, $Z$ = 2; $\rho_{calc}$ = 2.639 g/cc. This compound differs from its *anti*-isomer only in the coordination site of phosphine ligand on the triosmium cluster. The cluster contains a triangular arrangement of three osmium atoms, nine linear carbonyl ligands and a dimethylphenylphosphine ligand. A trifluoromethylalkylidenimino ($N{=}C(H)CF_3$) ligand symmetrically bridges one edge of the cluster via a nitrogen atom. The N=C bond is essentially double, 1.290(11) Å.

## Introduction

We recently reported on the reactions of the activated nitrile $CF_3CN$ with the clusters $H_2Os_3(CO)_9L$, L = CO, $PMe_2Ph$ [1]. The molecules $HOs_3[\mu\text{-}\eta^2\text{-}HN{=}CCF_3](CO)_9L$, L = CO, $PMe_2Ph$, and $HOs_3[\mu\text{-}\eta^1\text{-}N{=}C(H)CF_3](CO)_9L$, L = CO, I; $PMe_2Ph$, II, formed by the addition of one mole of nitrile to the cluster and the transfer of one hydride ligand either to the nitrogen atom or to the carbon atom, respectively, of the nitrile were isolated and characterized [1]. At the same time, we investigated the reaction of I with $PMe_2Ph$. We found that two non-interconvertible isomeric substitution products were formed. One of these was the same product II formed by the addition of $CF_3CN$ to $H_2Os_3(CO)_9PMe_2Ph$. The other which will be referred to hereafter as the *syn*-isomer has now been isolated, characterized by X-ray crystallographic methods and will be described here.

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## Experimental

### *General*

Preparation and purification was done under an atmosphere of prepurified nitrogen, although the compounds I and II (both *syn* and *anti*) were stable in air at room temperature. Hexane and heptane solvents were purified by distillation from sodium-benzophenone. Other solvents were stored over 4 Å molecular sieves. The preparation of $HOs_3[\mu\text{-}\eta^1\text{-}N{=}C(H)CF_3](CO)_{10}$ has been recently reported [1].

Dimethylphenylphosphine was obtained from Strem Chemicals Inc. Column chromatography was carried out on Baker acid-washed aluninum oxide, deactivated with 6% w/w water.

Infrared spectra were obtained from a Perkin-Elmer 237B spectrophotometer. A Bruker HX270 NMR instrument was used for obtaining $^1H$ NMR spectra at 270 MHz.

### *Reaction of $HOs_3[\mu\text{-}\eta^1\text{-}N{=}C(H)CF_3](CO)_{10}$ + $PMe_2Ph$*

$HOs_3[\mu\text{-}\eta^1\text{-}N{=}C(H)CF_3](CO)_{10}$, (65 mg, 0.060 mmol) and $PMe_2Ph$ (slight stoichiometric excess) were combined in 50 ml of heptane solvent under an atmosphere of nitrogen. The solution was refluxed for 2 hours. All volatile components from the reaction were removed under vacuum. An $^1H$ NMR spectrum of the residue showed that it contained nearly equal amounts of two hydride-containing species. One was *anti*-$HOs_3[\mu\text{-}\eta^1\text{-}N{=}C(H)CF_3](CO)_9PMe_2Ph$ [1]. The other was an isomer, *syn*-$HOs_3[\mu\text{-}\eta^1\text{-}N{=}C(H)CF_3](CO)_9PMe_2Ph$. The residue was chromatographed on an alumina column. A single yellow band was eluted with hexane/methylene chloride (10/1, v/v). This yellow band was crystallized from hexane solvent to yield yellow crystals. The two compounds could be isolated in pure form by separating crystals. The combined yield was 63.7 mg, 87%. IR ($\nu$(CO) $cm^{-1}$, in hexane solvent): 2096m, 2057s, 2020vs, 2007m, 1993w, 1987m, 1977m, 1960w. $^1H$ NMR (in $CDCl_3$), $\delta$ (in ppm), ($J$ in Hz): 7.83 d, q ($^4J(PH) \approx 4$, $^3J(FH) = 4.0$, CH); 7.28 m ($C_6H_5$), 1.97 d ($^2J = 9.7$, $CH_3$); 1.96 d ($^2J = 8.4$, $CH_3'$); —14.53 d ($^2J(P{-}H) = 8.9$, OsH).

### *Crystallographic analyses*

Crystals of *syn*-$HOs_3[\mu\text{-}\eta^1\text{-}N{=}C(H)CF_3](CO)_9PMe_2Ph$ suitable for diffraction measurements were obtained as described above and mounted in a thin-walled glass capillary. Diffraction measurements were made on an Enraf-Nonius CAD-4 fully automated four-circle diffractometer using graphite-monochromatized Mo-$K\bar{\alpha}$ radiation. The unit cell was determined and refined from 25 randomly selected reflections obtained using the CAD-4 automatic search, center, index and least-squares routines. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. Crystal data and data collection parameters are listed in Table 1. All data processing was performed on a Digital PDP 11/45 computer using the Enraf-Nonius SDP program library. An absorption correction of a Gaussian integration type was applied to all the data. Neutral atom scattering factors were calculated by the standard procedures [2a]. Anomalous dispersion corrections were applied for all nonhydrogen atoms [2b]. The structure was solved by a combination of Pat-

TABLE 1

CRYSTALLOGRAPHIC DATA FOR X-RAY DIFFRACTION STUDY OF *syn*-$HOs_3[\mu\text{-}\eta^1\text{-}N{=}C(H)CF_3](CO)_9PMe_2Ph$

| | |
|---|---|
| *A) Formula* | $Os_3PF_3O_9NC_{19}H_{13}$ |
| Temperature (±5°C) | 23 |
| Space group | $P\bar{1}$, No. 2 |
| *a* (Å) | 9.067(2) |
| *b* (Å) | 9.436(2) |
| *c* (Å) | 15.994(6) |
| α (deg) | 102.25(2) |
| β (deg) | 94.41(2) |
| γ (deg) | 92.26(2) |
| *V* (Å$^3$) | 1331.1(13) |
| M wt. | 1057.9 |
| $\rho_{calcd}$ (g/cc) | 2.639 |
| *B) Measurement of intensity data* | |
| Radiation | Mo-*K*α (0.71073 Å) |
| Monochromator | Graphite |
| Detector aperture (mm) | |
| Horizontal ($A + B \tan\theta$): | |
| *A* | 3.0 |
| *B* | 1.0 |
| Vertical: | 4.0 |
| Crystal faces: | $10\bar{1}$, $\bar{1}01$, $01\bar{1}$<br>$0\bar{1}1$, 111, $\bar{1}\bar{1}\bar{1}$ |
| Crystal size: (mm) | 0.14 × 0.33 × 0.35 |
| Crystal orientation: | |
| Direction; deg from φ-axis | normal to $\bar{1}\bar{1}\bar{2}$; 15.4° |
| Reflections measured | *h*, ±*k*, ±*l* |
| Max 2θ (°) | 50 |
| Scan type | moving crystal - stationary counter |
| ω-Scan width: | |
| $A + 0.347 \tan\theta$ | $A = 0.95°$ |
| Background: | 1/4 additional scan at each end of scan |
| ω-Scan rate (variable) | |
| max. (°/min) | 10.0 |
| min. (°/min) | 1.3 |
| No reflections measured | 4600 |
| Data used ($F^2 \geqslant 3.0\sigma(F)^2$) | 3571 |
| *C) Treatment of data* | |
| Absorption correction: | |
| Coefficient (cm$^{-1}$) | 153.2 |
| Grid | 8 × 8 × 14 |
| Transmission coefficient | |
| Max. | 0.154 |
| Min. | 0.026 |
| P-factor | 0.02 |
| Final residuals *R* | 0.045 |
| $R_w$ | 0.051 |
| E.s.d. of unit weight | 2.82 |
| Largest shift error value on final cycle | 0.02 |
| Largest peaks in final diff. Fourier ($e^-$/Å$^3$) | 1.4—1.6 |

terson and difference Fourier techniques. Hydrogen atom positions were obtained either from difference Fourier syntheses or calculated on the basis of geometric considerations. Hydrogen atom contributions were included in struc-

TABLE 2

POSITIONAL AND THERMAL PARAMETERS WITH ESTIMATED STANDARD DEVIATIONS FOR *syn*-$HOs_3[\mu\text{-}N{=}C(H)CF_3](CO)_9PMe_2Ph$ [a]

| Atom | $x/a$ | $y/b$ | $z/c$ | $B$ | Atom | $x/a$ | $y/b$ | $z/c$ | $B$ |
|---|---|---|---|---|---|---|---|---|---|
| Os(1) | 0.29528(6) | 0.14738(5) | 0.12760(3) | [b] | C(9) | 0.275(2) | 0.443(2) | 0.0066(11) | 5.0(3) |
| Os(2) | 0.20203(7) | 0.42697(5) | 0.11301(4) | [b] | C(10) | 0.484(2) | 0.280(2) | 0.2952(10) | 4.4(3) |
| Os(3) | 0.13457(6) | 0.30928(6) | 0.25699(4) | [b] | C(11) | −0.088(2) | 0.076(1) | 0.3495(9) | 4.1(3) |
| P | 0.0932(5) | 0.1711(4) | 0.3606(2) | [b] | C(12) | −0.183(2) | 0.094(2) | 0.4136(10) | 4.7(3) |
| F(1) | 0.658(1) | 0.413(1) | 0.4006(8) | [b] | C(13) | −0.320(2) | 0.004(2) | 0.3982(13) | 7.0(5) |
| F(2) | 0.442(1) | 0.489(1) | 0.3971(8) | [b] | C(14) | −0.356(2) | −0.094(2) | 0.3257(13) | 6.8(5) |
| F(3) | 0.487(2) | 0.301(1) | 0.4439(7) | [b] | C(15) | −0.266(2) | −0.111(2) | 0.2606(13) | 6.9(5) |
| O(1) | −0.193(1) | 0.337(1) | 0.2180(9) | 7.1(3) | C(16) | −0.132(2) | −0.024(2) | 0.2703(11) | 5.5(4) |
| O(2) | 0.144(2) | 0.605(1) | 0.3768(9) | 7.6(3) | C(17) | 0.216(2) | 0.023(2) | 0.3631(11) | 5.7(4) |
| O(3) | 0.581(1) | 0.208(1) | 0.0494(8) | 6.5(3) | C(18) | 0.110(2) | 0.270(2) | 0.4701(12) | 6.0(4) |
| O(4) | 0.148(1) | 0.035(1) | −0.0526(7) | 5.4(2) | C(19) | 0.342(2) | −0.038(1) | 0.1455(9) | 3.5(3) |
| O(5) | 0.372(1) | −0.154(1) | 0.1536(7) | 5.9(3) | H(10) | 0.5547 | 0.2207 | 0.2901 | 6.0 |
| O(6) | 0.493(1) | 0.552(1) | 0.2185(8) | 6.8(3) | H(12) | −0.1587 | 0.1662 | 0.4666 | 6.0 |
| O(7) | 0.047(2) | 0.711(1) | 0.1703(9) | 8.1(3) | H(13) | −0.3896 | 0.0157 | 0.4426 | 6.0 |
| O(8) | −0.090(1) | 0.267(1) | 0.0249(7) | 5.5(2) | H(14) | −0.4462 | −0.1564 | 0.3197 | 6.0 |
| O(9) | 0.319(2) | 0.450(1) | −0.0588(9) | 7.9(3) | H(15) | −0.2921 | −0.1841 | 0.2066 | 6.0 |
| N | 0.356(1) | 0.260(1) | 0.2518(7) | 3.2(2) | H(16) | −0.0700 | −0.0300 | 0.2221 | 6.0 |
| C(1) | −0.065(2) | 0.328(2) | 0.2324(11) | 5.8(4) | H(171) | 0.3047 | 0.0547 | 0.3750 | 6.0 |
| C(2) | 0.138(2) | 0.490(2) | 0.3327(11) | 5.4(4) | H(172) | 0.2123 | −0.0465 | 0.3038 | 6.0 |
| C(3) | 0.473(2) | 0.181(2) | 0.0784(10) | 4.4(3) | H(173) | 0.1933 | −0.0332 | 0.4052 | 6.0 |
| C(4) | 0.202(2) | 0.075(1) | 0.0149(9) | 3.8(3) | H(181) | 0.0567 | 0.3334 | 0.4805 | 6.0 |
| C(5) | 0.342(2) | −0.038(1) | 0.1455(9) | 3.5(3) | H(182) | 0.0840 | 0.2227 | 0.5215 | 6.0 |
| C(6) | 0.385(2) | 0.507(2) | 0.1781(10) | 4.6(3) | H(183) | 0.2141 | 0.2956 | 0.4719 | 6.0 |
| C(7) | 0.106(2) | 0.604(2) | 0.1453(11) | 5.8(4) | | | | | |
| C(8) | 0.019(2) | 0.324(1) | 0.0579(9) | 3.9(3) | | | | | |

| Atom | $B_{1,1}$ | $B_{2,2}$ | $B_{3,3}$ | $B_{1,2}$ | $B_{1,3}$ | $B_{2,3}$ |
|---|---|---|---|---|---|---|
| Os(1) | 2.91(2) | 2.61(2) | 2.30(2) | −0.20(2) | 0.41(2) | 0.27(1) |
| Os(2) | 3.90(2) | 2.80(2) | 3.59(2) | −0.01(2) | 0.95(2) | 0.95(2) |
| Os(3) | 3.38(2) | 3.50(2) | 2.67(2) | −0.03(2) | 0.96(2) | 0.43(2) |
| P | 4.3(2) | 4.8(2) | 2.2(1) | −0.5(1) | 0.7(1) | 0.6(1) |
| F(1) | 5.1(5) | 11.9(7) | 8.6(7) | −3.6(6) | −1.2(5) | −2.8(6) |
| F(2) | 10.8(7) | 9.2(6) | 8.3(6) | 2.5(6) | −4.5(6) | −4.0(5) |
| F(3) | 14(1) | 12.6(8) | 3.2(5) | −4.2(7) | 1.1(6) | −0.6(5) |

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[a] Hydrogen atoms were not refined. [b] Anisotropic thermal parameters. [c] The form of the anisotropic thermal parameter is $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + B_{12}hka^*b^* + B_{13}hla^*c^* + B_{23}klb^*c^*)]$.

TABLE 3

INTERATOMIC DISTANCES WITH E.s.d.s FOR *syn*-$HOs_3[\mu\text{-}N{=}C(H)CF_3](CO)_9PMe_2Ph$

| Atoms | Distance (Å) | Atoms | Distance (Å) |
|---|---|---|---|
| Os(1)—Os(2) | 2.835(1) | P—C(11) | 1.819(9) |
| Os(1)—Os(3) | 2.856(1) | P—C(17) | 1.827(10) |
| Os(2)—Os(3) | 2.852(1) | P—C(18) | 1.792(11) |
| Os(1)—C(1) | 1.845(12) | C(11)—C(12) | 1.38(1) |
| Os(1)—C(2) | 1.870(11) | C(12)—C(13) | 1.45(2) |
| Os(1)—P | 2.358(2) | C(13)—C(14) | 1.33(2) |
| Os(1)—N | 2.081(6) | C(14)—C(15) | 1.36(2) |
| Os(2)—C(3) | 1.893(10) | C(15)—C(16) | 1.42(2) |
| Os(2)—C(4) | 1.904(9) | C(16)—C(11) | 1.42(1) |
| Os(2)—C(5) | 1.893(8) | C(1)—O(1) | 1.18(1) |
| Os(2)—N | 2.065(16) | C(2)—O(2) | 1.16(1) |
| Os(3)—C(6) | 1.926(10) | C(3)—O(3) | 1.15(1) |
| Os(3)—C(7) | 1.910(11) | C(4)—O(4) | 1.13(1) |
| Os(3)—C(8) | 1.940(9) | C(5)—O(5) | 1.17(1) |
| Os(3)—C(9) | 1.903(11) | C(6)—O(6) | 1.14(1) |
| N—C(10) | 1.290(11) | C(7)—O(7) | 1.17(1) |
| C(10)—C(19) | 1.50(1) | C(8)—O(8) | 1.14(1) |
| C(19)—F(1) | 1.30(1) | C(9)—O(9) | 1.17(1) |
| C(19)—F(2) | 1.29(1) | | |
| C(19)—F(3) | 1.36(1) | | |

ture factor calculations, but their positions were not refined. Full-matrix least-squares refinements minimized the function $\Sigma_{hkl}\, w(|F_{obs}| - |F_{calc}|)^2$ where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F^2_{obs})/2\, F_{obs}$ and $\sigma(F^2_{obs}) = [\sigma(I_{raw})^2 + (PF^2_{obs})^2]^{1/2}/LP$. All atoms heavier than oxygen were refined with anisotropic temperature factors. All other atoms were refined with isotropic temperature factors only. Final fractional atomic coordinates, thermal parameters interatomic distances and angles with errors obtained from the inverse matrix calculated on the final cycle of least-squares refinement are listed in Tables 2—4. Structure factor amplitudes are available *.

## Results and discussion

An ORTEP diagram of the molecular structure of *syn*-$HOs_3[\mu\text{-}\eta^1\text{-}N{=}C(H)CF_3](CO)_9PMe_2Ph$ is shown in Fig. 1. For comparative purposes an ORTEP diagram of *anti*-$HOs_3[\mu\text{-}\eta^1\text{-}N{=}C(H)CF_3](CO)_9PMe_2Ph$ as obtained from the addition of $CF_3CN$ to $H_2Os_3(CO)_9PMe_2Ph$, is shown in Fig. 2 [1]. The basic difference between the molecules is the site of substitution of the phosphine ligand on the cluster. In the *syn*-isomer the phosphine is coordinated to the osmium atom positioned *syn* to the $CF_3$ group while in the *anti* isomer the phosphine ligand is coordinated to the osmium atom positioned *anti* to the $CF_3$ group. Both isomers contain triangular clusters of three osmium atoms. As

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* The table of final observed and calculated structure factor amplitudes has been deposited as NAPS Document No. 03863 (16 pages). Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. A copy may be secured by citing the document number, remitting $7.75 for photocopies or $3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publication.

TABLE 4

INTERATOMIC ANGLES WITH E.s.d.s FOR *syn*-$HOs_3[\mu\text{-}\eta^1\text{-}N{=}C(H)CF_3](CO)_9PMe_2Ph$

| Atoms | Angle (degrees) | Atoms | Angle (degrees) |
|---|---|---|---|
| Os(1)—Os(2)—Os(3) | 60.29(1) | Os(2)—Os(3)—C(7) | 156.4(3) |
| Os(1)—Os(3)—Os(2) | 59.55(1) | Os(2)—Os(3)—C(8) | 85.4(2) |
| Os(2)—Os(1)—Os(3) | 60.15(1) | Os(2)—Os(3)—C(9) | 100.9(3) |
| Os(2)—Os(1)—C(1) | 118.6(3) | C(6)—Os(3)—C(7) | 92.8(4) |
| Os(2)—Os(1)—C(2) | 141.7(3) | C(6)—Os(3)—C(8) | 171.3(4) |
| Os(2)—Os(1)—P | 109.32(6) | C(6)—Os(3)—C(9) | 93.1(4) |
| Os(2)—Os(1)—N | 46.6(2) | C(7)—Os(3)—C(8) | 91.9(4) |
| Os(3)—Os(1)—C(1) | 90.6(4) | C(7)—Os(3)—C(9) | 102.7(5) |
| Os(3)—Os(1)—C(2) | 94.5(3) | C(8)—Os(3)—C(9) | 93.0(4) |
| Os(3)—Os(1)—P | 169.25(6) | Os(1)—N—Os(2) | 86.3(2) |
| Os(3)—Os(1)—N | 80.6(2) | Os(1)—N—C(10) | 143.5(6) |
| C(1)—Os(1)—C(2) | 87.3(5) | Os(2)—N—C(10) | 130.2(6) |
| C(1)—Os(1)—P | 93.3(4) | N—C(10)—C(19) | 125.6(9) |
| C(1)—Os(1)—N | 165.2(4) | F(1)—C(19)—C(10) | 113(1) |
| C(2)—Os(1)—P | 109.32(6) | F(2)—C(19)—C(10) | 114(1) |
| C(2)—Os(1)—N | 105.1(4) | F(3)—C(19)—C(10) | 110(1) |
| P—Os(1)—N | 93.5(2) | F(1)—C(19)—F(2) | 109(1) |
| Os(1)—Os(2)—C(3) | 135.2(3) | F(1)—C(19)—F(3) | 103(1) |
| Os(1)—Os(2)—C(4) | 120.2(3) | F(2)—C(19)—F(3) | 106(1) |
| Os(1)—Os(2)—C(5) | 114.1(3) | Os(1)—P—C(11) | 115.9(3) |
| Os(1)—Os(2)—N | 47.1(2) | Os(1)—P—C(17) | 115.8(4) |
| Os(3)—Os(2)—C(3) | 90.8(3) | Os(1)—P—C(18) | 115.8(4) |
| Os(3)—Os(2)—C(4) | 87.5(2) | C(11)—P—C(17) | 101.2(5) |
| Os(3)—Os(2)—C(5) | 174.1(3) | C(11)—P—C(18) | 103.2(5) |
| Os(3)—Os(2)—N | 81.0(2) | C(17)—P)C(18) | 102.8(5) |
| C(3)—Os(2)—C(4) | 87.5(2) | C(11)—C(12)—C(13) | 118(1) |
| C(3)—Os(2)—C(5) | 94.8(4) | C(12)—C(13)—C(14) | 123(1) |
| C(3)—Os(2)—N | 98.7(3) | C(13)—C(14)—C(15) | 121(1) |
| C(4)—Os(2)—C(5) | 94.4(3) | C(14)—C(15)—C(16) | 120(1) |
| C(4)—Os(2)—N | 166.3(3) | C(15)—C(16)—C(11) | 120(1) |
| Os(1)—Os(3)—C(6) | 87.2(3) | C(16)—C(11)—C(12) | 119(1) |
| Os(1)—Os(3)—C(7) | 96.9(3) | Os(1)—C(1)—O(1) | 179(1) |
| Os(1)—Os(3)—C(8) | 85.0(3) | Os(1)—C(2)—O(2) | 177(1) |
| Os(1)—Os(3)—C(9) | 160.4(3) | Os(2)—C(3)—O(3) | 177(1) |
| Os(2)—Os(3)—C(6) | 87.3(3) | Os(2)—C(4)—O(4) | 179(1) |
| | | Os(2)—C(5)—O(5) | 178(1) |
| | | Os(3)—C(6)—O(6) | 178(1) |
| | | Os(3)—C(7)—O(7) | 176(1) |
| | | Os(3)—C(8)—O(8) | 178(1) |
| | | Os(3)—C(9)—O(9) | 179(1) |

in the *anti*-isomer [1], the bridged osmium—osmium bond in the *syn*-isomer is slightly shorter, Os(1)—Os(2) = 2.835(1) Å, than the other two, Os(1)—Os(3) = 2.856(1) Å and Os(2)—Os(3) = 2.852(1) Å, and all are only slightly shorter than those found in $Os_3(CO)_{12}$, 2.877(3) Å [3]. Churchill has shown previously that the bridged metal—metal bond distance in triosmium clusters, in which the bridge consists of a single heteroatom, is frequently shorter than or equal to the unbridged metal—metal bond distances [4].

The alkylidenimino ligand, $N{=}C(H)CF_3$, symmetrically bridges the Os(1)—Os(2) bond via the nitrogen atom, Os(1)—N = 2.081(6) Å and Os(2)—N = 2.065(6) Å, and serves formally as a three-electron donor. The iminyl bond C(10)—N is formally double. This is supported by the short internuclear separa-

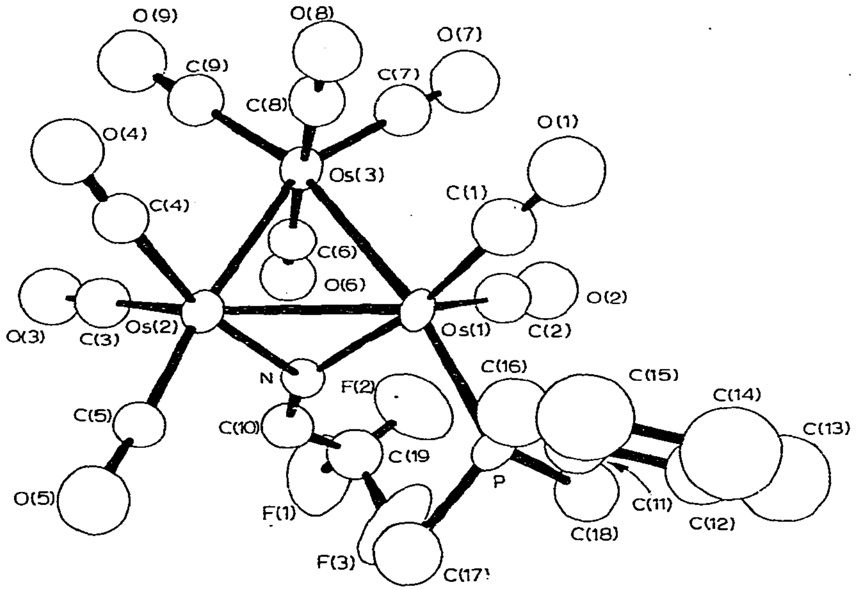

Fig. 1. An ORTEP diagram of *syn*-$HOs_3[\mu\text{-}\eta^1\text{-}N{=}C(H)CF_3](CO)_9PMe_2Ph$, showing 50% probability ellipsoids.

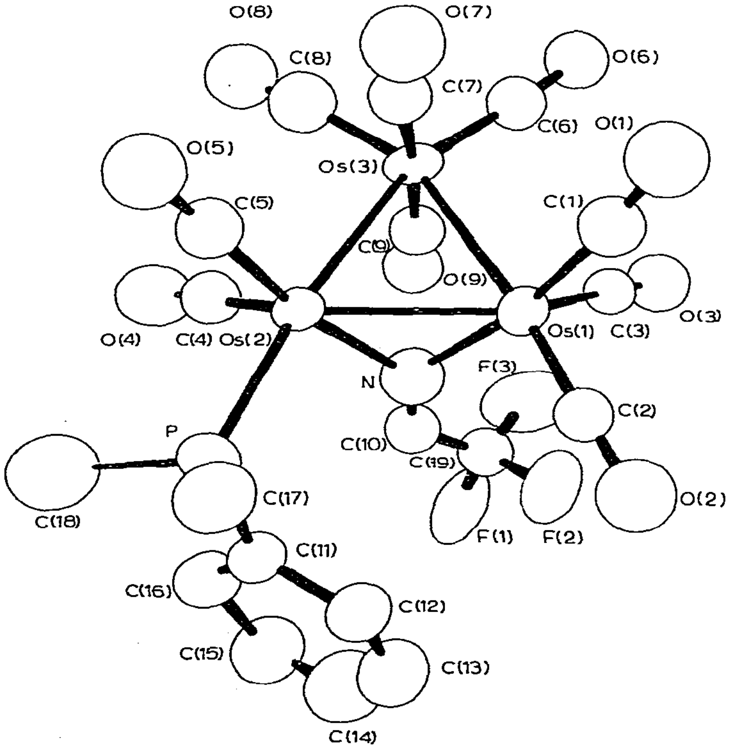

Fig. 2. An ORTEP diagram of *anti*-$HOs_3[\mu\text{-}\eta^1\text{-}N{=}C(H)CF_3](CO)_9PMe_2Ph$, showing 50% probability ellipsoids.

tion of 1.290(11) Å and the non-interconvertibility of the isomers, which could otherwise be achieved by a simple 180° rotation about the C(10)—N bond. As expected, the corresponding C—N bond distance in the *anti*-isomer was also found to be characteristically short (i.e. 1.247(15) Å [1]). Other molecules containing alkylidenimino ligands with short C—N bonds are $Mn_2[\mu-\eta^1-N=C(CF_3)_2](CO)_7$, C—N = 1.259(9) and 1.258(9) Å [5], and $Fe_2[\mu-\eta^1-N=C(p\text{-tolyl})_2]_2$, C—N = 1.24(2) and 1.29(2) Å [6]. In $Re_2[\mu-\eta^1-N=C(H)Me](CO)_6$ dpm a longer C—N distance of 1.39(6) Å was observed but the e.s.d. on that determination is rather large [7]. The hydrogen atom on C(10) was not observed crystallographically, but its location at that site is supported by $^1H$ NMR spectroscopy which shows a low-field multiplet $\delta = 7.83$ ppm of intensity one which is coupled to the $CF_3$ fluorines, $J(F—H) = 4.0$ Hz, and the phosphine ligand, $J(P—H) = 4.0$ Hz. The N—C(10)—C(19) angle at 125.6(9)° is slightly larger than that found in the *anti*-isomer (121.7(14)°). The hydride ligand was observed spectroscopically, $\delta = -14.53$ ppm $J(P—H) = 8.9$ Hz. It was not observed crystallographically, but it is believed to bridge the Os(1)—Os(2) bond on the opposite side of the cluster to the alkylidenimino ligand in the cavity circumscribed by the ligands C(1)—O(1), C(4)—O(4), C(5)—O(5) and the phosphine. There are nine linear carbonyl ligands (M—C—O angles range from 175—179°) distributed such that Os(3) has four, Os(2) has three and Os(1) has two. Complete lists of interatomic bond distances and angles are given in Tables 3 and 4.

In the crystal this *syn*-isomer consists of discrete molecules. The shortest intermolecular contacts are between fluorine atoms at 2.881(9) Å.

In summary, the two products formed by the addition of $PMe_2Ph$ to $HOs_3[\mu-\eta^1-N=C(H)CF_3](CO)_{10}$ are substitutional isomers which differ only in the location of the phosphine ligand in the cluster. In each product substitution has occurred on the ligand-bridged osmium atoms. Whether or not this is due to some sort of labilizing influence caused by the bridging ligand remains to be established, but such behavior has been observed or can be inferred from studies on other triosmium cluster complexes. For example, phosphine substitution occurs at the bridged osmium atoms in the molecules $HOs_3(\mu-SPh)(CO)_{10}$ [8]. Under a CO atmosphere ligand exchange occurs preferentially at the bridged osmium atoms in the molecule $Os_3(\mu-X)_2(CO)_{10}$, X = halide [9]. In the molecule $HRu_3(\mu-\eta^1-C=NMe_2)(CO)_{10}$, Churchill described a structural *trans* effect in which CO ligands *trans* to the bridging ligand contained significantly elongated metal—carbon bond distances [10].

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