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The activation of tertiary amines by osmium cluster complexes: Further studies of the reaction of $Os_3(CO)_{10}(NCMe)_2$ with triethylamine

Richard D Adams* and James T Tanner
Department of Chemistry, University of South Carolina, Columbia, SC 29208, USA

The reactions of $Os_3(CO)_{12}$ and $Os_3(CO)_{10}(NCMe)_2$ with NEt_3 have been reinvestigated. Two new products, $Os_3(CO)_{10}(\mu\text{-}CH_2C(H){=}NEt_2)(\mu\text{-}H)$ (2) and $Os_3(CO)_{10}(syn\text{-}\mu\text{–}\eta^1\text{-}CHCHNEt_2)(\mu\text{-}H)$ (3) were obtained in low yields, 4% and 7%, in addition to the previously reported compound $Os_3(CO)_{10}(anti\text{-}\mu\text{–}\eta^1\text{-}CHCHNEt_2)(\mu\text{-}H)$ (1) (20% yield) when the reaction was conducted at 25 °C using $Os_3(CO)_{10}(NCMe)_2$. Compounds 2 and 3 were characterized by IR, ^1H NMR and single-crystal X-ray diffraction analyses. Compound 2 contains a bridging methyl-metallated *N*-ethylimine ligand formed by the cleavage of one ethyl group from the NEt_3. Compound 3 is an isomer of 1 in which the bridging ligand has a *syn* conformation with respect to the cluster as compared with the *anti* conformation in 1. Compound 3 slowly isomerizes to 1. Compound 3 is decarbonylated by exposure to UV radiation and is transformed to the new compound $Os_3(CO)_9(\mu_3\text{-}CC(H){=}NEt_2)(\mu\text{-}H)_2$ (4) (58% yield) by an additional CH activation to form a triply bridging η^1-diethylaminovinylidene ligand. Compound 4 isomerizes to the compound $Os_3(CO)_9(\mu_3\text{-}HCCNEt_2)(\mu\text{-}H)_2$ (5) (70% yield) at 68 °C. The latter contains a triply briding ynamine ligand which exhibits structural and reactivity features that are characteristic of a carbene ligand at the amine-substituted carbon atom. Crystal data: for 2, space group = $P2_1/c$, $a = 9.236(2)$ Å, $b = 12.469(2)$ Å, $c = 18.107(3)$ Å, $\beta = 104.67(1)$ °, $Z = 4$, 2518 reflections, $R = 0.031$; for 3, space group = $P2_1/m$, $a = 7.644(1)$ Å, $b = 12.706(2)$ Å, $c = 11.912(2)$ Å, $\beta = 108.02(1)$ °, $Z = 2$, 1295 reflections, $R = 0.030$; for 4, space group = $P2_1/n$, $a = 10.233(2)$ Å, $b = 14.834(4)$ Å, $c = 14.538(2)$ Å, $\beta = 99.88(2)$ °, $Z = 4$, 2403 reflections, $R = 0.036$.

Keywords: Cluster, osmium, tertiary amine, C–H activation, C–N activation, triethylamine

INTRODUCTION

Understanding the nature of carbon–hydrogen bond activation and carbon–nitrogen bond cleavage processes in the reactions of polynuclear metal complexes with tertiary amines has been a major goal of our research in recent years. Both C–H activation and C–N bond cleavage are integral steps in the industrially important hydrodenitrification process in which nitrogen is removed from heterocyclic organonitrogen compounds in petroleum crude via heterogeneous metal-promoted hydrogenation.[1–5] The mechanism by which these steps occur is poorly understood, and a considerable amount of research has been devoted to modeling this heterogeneous reaction by using homogeneous catalysts.[6–14] Laine and co-workers[10–14] have shown in their studies on C–H and C–N bond activations in saturated tertiary amines that there is a good correlation between the reactivity of homogeneous metal cluster catalysts and heterogeneous catalysts in the deuterium–hydrogen exchange reaction (Eqn [1]) and the alkyl exchange reaction (Eqn [2]) involving tertiary amines.

$$D_2O + Et_3N \xrightarrow{Ru_3(CO)_{12}} Et_2NCHDCD_3 \qquad [1]$$

$$Et_3N + Pr_3N \xrightarrow{Os_3(CO)_{12}} Et_2NPr + Pr_2NEt \qquad [2]$$

Whilst these studies have produced substantial advances in understanding the nature of C–H activation in tertiary amines, a major impediment to obtaining detailed mechanistic information has been the lack of isolable intermediates.

Recent studies in our laboratory have focused on the C–H and C–N bond cleavage reactions in tertiary amines by osmium and ruthenium carbonyl cluster complexes.[15] We have shown that

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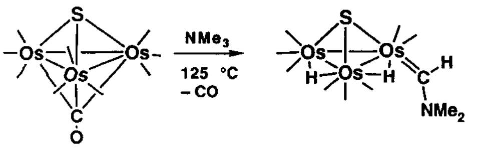
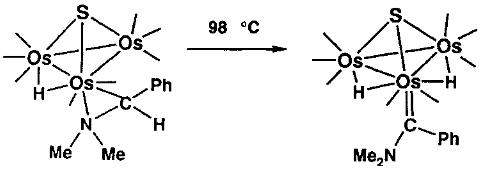
trimethylamine can be transformed into a dimethylaminocarbene ligand by a double C–H activation on one of its *N*-methyl groups (Eqn [3]).[16]



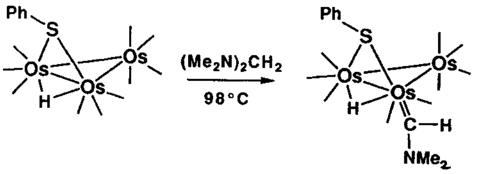
[3]

The reaction is believed to occur through a sequence of C–H activations on the methyl group and may traverse an intermediate containing a π-complexed iminium ligand. In support of this we have shown that the π-iminium complex $Os_3(CO)_8[\eta^2\text{-}C(H)Ph{=}NMe_2](\mu_3\text{-}S)(\mu H)$ is converted to the analogous carbene complex $Os_3(CO)_8[C(Ph)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ (Eqn [4]).[17]



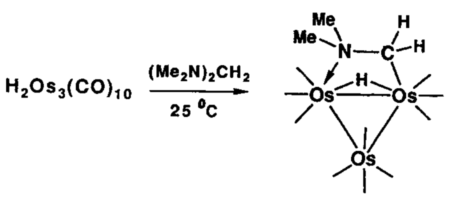
[4]

The diamine, *N*,*N*,*N*′,*N*′-tetramethyldiaminomethane, also undergoes facile C–H and C–N bond cleavage to yield carbene complexes (Eqn [5]).[18,19]



[5]

In another case, direct C–N cleavage in the diamine molecule was observed at ambient temperature to yield the first example of a cluster complex containing a μ_2-iminium ligand (Eqn [6]).[20]



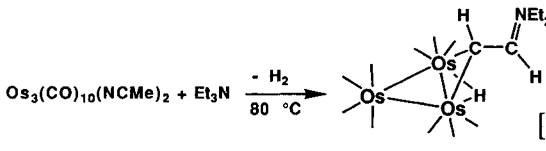
[6]

Recently we have shown that the cluster complex $Os_3(CO)_8(C(H)NMe_2)(\mu\text{-}H)_2$ can catalyze the alkyl exchange reaction (Eqn [7]).

$$Et_3N + Pr_3N \overset{H_2Os_3(CO)_8(C(H)NMe_2)}{\rightleftharpoons} Et_2NPr + Pr_2NEt \quad [7]$$

A detailed mechanistic study of this reaction has shown that the carbene ligand is involved in C–N bond cleavage during the reaction.

In 1978 Shapley reported the formation of the unusual complex $Os_3(CO)_{10}$(*anti*-μ-$CHCHNEt_2$)(μ-H) (**1**) from the reaction of $Os_3(CO)_{10}(NCMe)_2$ with NEt_3 in refluxing benzene solvent (Eqn [8]).[22,23] Complex **1** contained a novel 1,3-dipolar $^-CHCH{=}NEt_2^+$ iminium ligand formed by the abstraction of three hydrogen atoms from one of the ethyl groups of the NEt_3 molecule. One hydrogen atom became the hydride ligand. The other two hydrogen atoms were found in the coproduct, $Os_3(CO)_{10}(\mu\text{-}H)_2$. Rosenberg *et al.* have recently shown that similar products are obtained from the reaction of $Os_3(CO)_{10}(NCMe)_2$ with secondary amines.[24]



[8]

We have now reinvestigated the reaction of NEt_3 with $Os_3(CO)_{10}(NCMe)_2$. We have isolated an intermediate en route to **1**, and have also isolated a side-product formed by the cleavage of one of the ethyl groups from the NEt_3 molecule, but more importantly we have found that **1** can be decarbonylated in a process that leads to further activation of the C–H bonds on the transformed ethyl group. Our studies of the preparation, structural characterization and reactivity of these compounds are reported here. A preliminary report of this work has been published.[25]

EXPERIMENTAL

General methods

Although the reaction products are air-stable, all the reactions were performed under an atmosphere of nitrogen unless otherwise indicated. Triethylamine was purchased from Aldrich and was purified and dried by established methods before use.[26] Methylene chloride was freshly distilled from calcium hydride before use. Technical grade octane was purchased from Phillips Co. and purified by treatment with sulfuric acid and distillation before use. Reagent-grade toluene was freshly distilled from sodium/benzophenone before use. $Os_3(CO)_{10}(NCMe)_2$ was prepared by the published procedure.[27] IR spectra were recorded on a Nicolet 5DXB FT-IR spectrophotometer. ^{1}H NMR spectra were recorded on a Brüker AM-300 spectrometer of a Brüker AM-500 spectrometer. Variable-temperature spectra were recorded on an IBM-NR80 spectrometer. Elemental analyses were performed at Desert Analytics, Tucson, AZ, USA. TLC separations were performed on plates (0.25 mm Kieselgel 60 F_{254}, from E. Merck, Germany).

Reaction of $Os_3(CO)_{10}(NCMe)_2$ with triethylamine at 25 °C

$Os_3(CO)_{10}(NCMe)_2$ (100 mg; 0.107 mmol) was dissolved in 65 cm^3 of toluene, and 0.5 cm^3 of triethylamine was added from a syringe. The solution was stirred under a nitrogen atmosphere for 24 h at 25 °C. At this time the solution was orange. The solvent was removed *in vacuo*. The orange residue was dissolved in a minimum of CH_2Cl_2 and chromatographed by TLC using a 4 : 1 hexane/CH_2Cl_2 solvent mixture. This yielded the following bands in order of elution: 4.0 mg of $Os_3(CO)_9(\mu\text{-}CH_2CH{=}NEt)(\mu\text{-}H)$, **2** as a pale yellow band (4 %), 7.0 mg of $Os_3(CO)_{10}(syn\text{-}\mu\text{-}\eta^1\text{-}CHCHNEt_2)(\mu\text{-}H)$, **3** as an orange band (7 %), 20.0 mg of the known compound $Os_3(CO)_{10}(anti\text{-}\mu\text{-}\eta^1\text{-}CHCHNEt_2)(\mu\text{-}H)$, **1** (20 %) as an orange band and 10 mg of the known compound $Os_3(CO)_{10}(\mu\text{-}OH)(\mu\text{-}H)$ as a yellow band (11 %).

For **2**: IR νCO in hexane (cm^{-1}): 2102 (w), 2060 (vs), 2049 (s), 2025 (m, sh), 2020 (vs), 2001 (m, sh), 1996 (vs), 1989 (s), 1971 (w). ^{1}H NMR (δ in $CDCl_3$): 9.13 (m, 1H), 3.77 (q, 2H, $J_{H\text{-}H}$ = 7.5 Hz), 2.35 (d, 1H, $J_{H\text{-}H}$ = 21.5 Hz), 1.73 (d, 1H, $J_{H\text{-}H}$ = 21.5 Hz), 1.19 (t, 3H, $J_{H\text{-}H}$ = 7.5 Hz), −14.27 (s, 1H, $J_{H\text{-}H}$ = 21.5 Hz). Analysis: Calcd, C, 18.24; N, 1.52; H, 1.00. Found, C, 18.37; N, 1.58; H, 0.93.

For **3**: IR νCO in hexane (cm^{-1}): 2094 (w), 2049 (vs), 2041 (m, sh), 2012 (s), 1997 (m, sh), 1989 (s), 1979 (s), 1967 (w). ^{1}H NMR (δ in $CDCl_3$): 8.62 (d, 1H, $J_{H\text{-}H}$ = 15.2 Hz), 5.01 (dd, 1H, $J_{H\text{-}H}$ = 12.5 Hz), 3.37 (q, 4H, $J_{H\text{-}H}$ = 7.4 Hz), 1.29 (t, 6H, $J_{H\text{-}H}$ = 7.4 Hz), −15.98 (d, 1H, $J_{H\text{-}H}$ = 1.8 Hz). Analysis Calcd, C, 20.23, N, 1.47, H, 1.38. Found, C, 20.95, N, 1.51, H, 1.30%.

Pyrolysis of compound 3 at 68 °C

Compound **3** (15 mg; 0.016 mmol) was dissolved in 20 cm^3 of hexane. The solution was refluxed for 15 min. At this time an IR spectrum of the solution indicated complete conversion of **3** to **1**. The solvent was removed *in vacuo* to yield 12.0 mg of **1** (80 %).

Photolysis of compound 1

A 100 mg (0.105 mmol) portion of **1** was dissolved in 100 cm^3 of hexane. The orange solution was irradiated with UV radiation by using a high-pressure mercury lamp (externally positioned) for 2.5 h in the presence of a slow purge of nitrogen through the solution. After this time the solution was bright yellow and an IR spectrum of the solution showed that no starting material remained. The solvent was removed *in vacuo*. The yellow residue was dissolved in a minimum of CH_2Cl_2 and chromatographed by TLC using a 4 : 1 hexane/CH_2Cl_2 solvent mixture. This yielded the following bands in order of elution: 20 mg of $Os_3(CO)_9(\mu_3\text{-}HCCNEt_2)(\mu\text{-}H)_2$ (**5**) as a UV band (21 %), and 56 mg of $Os_3(CO)_9(\mu_3\text{-}CCHNEt_2)(\mu\text{-}H)_2$ (**4**) as a yellow band (58 %).

For **4**: IR νCO in hexane (cm^{-1}): 2096 (m), 2064 (vs), 2037 (vs), 2018 (s), 2009 (m), 1982 (s), 1971 (m), 1957 (w). ^{1}H NMR (δ in $CDCl_3$): 9.10 (s, 1H), 3.61 (q, 2H $J_{H\text{-}H}$ = 7.2 Hz), 3.53 (q, 2H, $H_{H\text{-}H}$ = 7.2 Hz), 1.28 (t, 6H, $J_{H\text{-}H}$ = 7.2 Hz), −19.31 (s, 2H). Analysis: Calcd, C, 19.54; N, 1.52; H, 1.42. Found, C, 19.67; N, 1.50; H, 1.35 %.

For **5**: IR νCO in hexane (cm^{-1}): 2101 (m), 2071 (vs), 2045 (vs), 2018 (sh), 2015 (s), 2000 (s), 1982 (s), 1977 (w, sh), 1967 (m). ^{1}H NMR (δ in $CDCl_3$): 5.87 (s, 1H), 3.91 (q, 2H, $J_{H\text{-}H}$ = 7.4 Hz), 3.54 (q, 2H, $J_{H\text{-}H}$ = 7.4 Hz), 1.28 (t, 3H, $J_{H\text{-}H}$ = 7.4 Hz), 1.22 (t, 3H, $J_{H\text{-}H}$ = 7.4 Hz), −16.35 (s, br, 1H), −18.90 (s, br, 1H). Analysis: Calcd, C, 19.54; N, 1.52; H, 1.42. Found, C, 19.75; N, 1.50; H, 1.34 %.

Pyrolysis of 4 at 68 °C

Compound **4** (50 mg; 0.054 mmol) was dissolved in 50 cm^3 of hexane. The light yellow solution was refluxed for 3 h. The solution slowly changed from light yellow to almost colorless. An IR spectrum of the solution showed that no compound **4** remained. Removal of the solvent and work-up as before yielded 35 mg of **5** (70 %).

Table 1 Crystallographic data for diffraction studies

Compound			
Empirical formula	**2**	**3**	**4**
Formula weight	$Os_3O_{10}NC_{14}H_9$	$Os_3O_{10}NC_{16}H_{13}$	$Os_3O_9NC_{15}H_{13}$
Crystal system	921.83	949.88	921.87
Lattice parameters	Monoclinic	Monoclinic	Monoclinic
a, Å	9.236(2)	7.644(1)	10.233(2)
b, Å	12.469(2)	12.706(2)	14.834(4)
c, Å	18.107(3)	11.912(2)	14.538(2)
β, deg	104.67(1)	108.02(1)	99.88(2)
V, $Å^3$	2017(1)	1100.2(7)	2174.2(8)
Space group	$P2_1/c$ (No. 14)	$P2_1/m$(No. 11)	$P2_1/n$ (No. 14)
Z	4	2	4
D_{calc} ($g\,cm^{-3}$)	3.04	2.87	2.82
F_{000}	1632	848	1640
μ(MoKα), cm^{-1}	189.2	173.5	185.7
Radiation	Mc Kα ($\lambda = 0.71069$)	Ma Kα ($\lambda = 0.71069$)	Mo Kα ($\lambda = 0.71069$)
Abs. corr.	Empirical	Analytical	Analytical
Temp, °C	20	20	20
$2\theta_{max}$, deg.	47.0	46.0	45.0
No. of observations ($I > 3\sigma(I)$)	2518	1295	2403
No. of variables	256	168	136
Residuals: R; R_w	0.031; 0.034	0.030; 0.032	0.036; 0.040
Goodness of fit indicator	1.70	1.59	2.12
Max. shift in final cycle	0.03	0.06	0.26
Largest peak in final diff. map, e $Å^{-3}$	1.41	1.01	1.05

Reaction of $Os_3(CO)_{12}$ with NEt_3 at 125 °C

$Os_3(CO)_{12}$ (60 mg; 0.066 mmol) was dissolved in 60 cm^3 of octane in a three-necked 100-cm^3 round-bottomed flask fitted with a reflux condenser and rubber septa. A second two-neck 25-cm^3 round-bottomed flask containing 20 cm^3 of triethylamine was connected to the 100 cm^3 flask via a glass pipet and tygon tubing. The $Os_3(CO)_{12}$/octane solution was brought to reflux. A slow purge of nitrogen bubbling through the 25-cm^3 flask was used to carry a small flow of triethylamine vapor through the refluxing solution. Reflux was maintained for 5 h, at which time an IR spectrum of the reaction mixture indicated no $Os_3(CO)_{12}$ remained. The solvent was removed *in vacuo*. The yellow residue was dissolved in a minimum of CH_2Cl_2 and chromatographed by TLC using a 4:1 hexane/CH_2Cl_2 solvent mixture. This yielded compound **5** as the major product (15 mg; 25 %). Other trace bands were observed on the plate. These products were not characterized.

Reaction of 5 with NPr_2H

Compound **5** (75 mg; 0.081 mmol) was dissolved in 60 cm^3 of heptane. Excess (0.25 cm) of dipropylamine was added to the solution via a syringe. The solution was brought to reflux and maintained for a total of 5 h. During this time the reaction was monitored by TLC using 0.5-cm^3 aliquots of the reaction mixture. Over this period of time, a new UV band eluting faster than **5** appeared and grew in intensity. At the end of 5 h, compound **5** was nearly absent. The solvent was removed *in vacuo*. The pale yellow residue was dissolved in a minimum of CH_2Cl_2 and chromatographed by TLC using a 7:3 hexane/CH_2Cl_2 solvent mixture. This yielded the following bands in order of elution: $Os_3(CO)_9(\mu_3\text{-}HCCNPr_2)(\mu\text{-}H)_2$, **6** (56 mg; 74 %) eluting as a UV band, and 11.8 mg of unreacted **5**.

For **6**: IR νCO in hexane (cm^{-1}): 2101 (m), 2072 (vs), 2045 (vs), 2018 (sh), 2015 (vs), 2000 (s), 1982 (s), 1977 (w, sh), 1967 (m). ^1H NMR (δ in $CDCl_3$): 5.84 (s, 1H), 3.48 (t, 2H, $J_{H\text{-}H} = 7.8$ Hz),

Table 2 Positional parameters and B(eq) values for compound **2**

Atom	x	y	z	B (eq)
Os(1)	0.71709(06)	0.13621(04)	0.43413(03)	3.34(2)
Os(2)	0.76267(05)	0.36745(04)	0.44086(03)	3.12(2)
Os(3)	0.64391(05)	0.26455(03)	0.29438(03)	2.59(2)
O(11)	1.0446(13)	0.0873(09)	0.4332(07)	7.6(6)
O(12)	0.6493(14)	−0.1013(08)	0.4179(06)	6.6(6)
O(13)	0.7736(14)	0.1381(08)	0.6059(06)	7.1(6)
O(21)	0.4375(11)	0.4050(08)	0.4492(06)	6.0(5)
O(22)	0.7895(11)	0.6004(08)	0.3940(06)	6.1(5)
O(23)	1.0881(11)	0.3289(10)	0.4325(07)	6.9(6)
O(24)	0.8662(12)	0.3940(09)	0.6140(06)	6.5(6)
O(31)	0.9564(11)	0.2478(10)	0.2735(06)	7.2(6)
O(32)	0.5412(11)	0.1559(08)	0.1381(05)	5.7(5)
O(33)	0.6152(12)	0.4913(08)	0.2312(06)	6.1(5)
N	0.4193(10)	0.2554(08)	0.3073(06)	3.3(4)
C(1)	0.3786(15)	0.2034(10)	0.3585(08)	4.2(6)
C(2)	0.4782(14)	0.1533(10)	0.4277(07)	3.9(6)
C(3)	0.2917(14)	0.2975(11)	0.2456(08)	4.4(6)
C(4)	0.2515(19)	0.4095(11)	0.2618(09)	6.0(8)
C(11)	0.9246(18)	0.1105(10)	0.4318(08)	4.6(6)
C(12)	0.6753(16)	−0.0099(11)	0.4228(07)	4.2(6)
C(13)	0.7534(17)	0.1384(10)	0.5406(08)	4.6(6)
C(21)	0.5555(16)	0.3870(10)	0.4441(08)	4.2(6)
C(22)	0.7747(14)	0.5143(12)	0.4115(08)	4.5(6)
C(23)	0.9671(15)	0.3409(11)	0.4328(07)	4.2(6)
C(24)	0.8293(14)	0.3800(10)	0.5486(08)	4.1(6)
C(31)	0.8415(16)	0.2557(11)	0.2833(06)	4.2(6)
C(32)	0.5722(13)	0.1950(10)	0.1978(07)	3.6(5)
C(33)	0.6233(13)	0.4075(10)	0.2564(07)	3.8(6)
H(1)	0.673(11)	0.141(07)	0.326(05)	3.0

3.40 (t, 2H, $J_{H\text{-}H}=7.8$ Hz), 1.66 (m, 4H), 0.96 (t, 3H, $J_{H\text{-}H}=5.8$ Hz), 0.94 (t, 3H, $J_{H\text{-}H}=5.8$ Hz), −16.35 (s, br, 1H), −18.90 (s, br, 1H).

Reaction of 5 with NPr_3

A 46 mg portion of **5** (0.05 mmol) was dissolved in 60 cm^3 of heptane. An excess of NPr_3(1.0 cm^3) was added to the solution via a syringe, and the solution was refluxed for 10 h. After this time the solution was slightly brown in color. The solvent was then removed *in vacuo*, and the yellow-brown residue was separated as described above to yield 10.5 mg of **6** as a UV band (37 % based on the amount of **5** consumed), and 21 mg of unreacted **5**.

Crystallographic analyses

Crystals of compounds **2**, **3**, and **4** suitable for diffraction analyses were grown from solutions in hexane/CH_2Cl_2 solvent mixtures at −10 °C. The data crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer using graphite-monochromatized MoKα radiation. Unit cells were determined and refined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table 1. All data processing was performed on a Digital Equipment Corp. MICROVAX II or a VAXstation 3520 computer by using the TEXSAN structure-solving program library obtained from the Molecular Structure Corp., The Woodlands, TX, USA. Lorentz/polarization (Lp) corrections were applied. Neutral atom scattering factors were obtained from the standard sources. Anomalous dispersion corrections were applied to all non-hydrogen atoms. Full matrix least-squares refinement minimized the function:

$$\Sigma_{hkl}\, w(|F_0| - |F_c|)^2$$

where

$$w = 1/\sigma(F)^2,\ \sigma(F) = \sigma(F_0^2)/2F_0$$

and

$$\sigma(F_0^2) = [\sigma(I_{\mathrm{raw}})^2 + (0.02I_{\mathrm{net}}^2)]^{1/2}/\mathrm{L}p$$

Compound **2** crystallized in the monoclinic crystal system. The space group $P2_1/c$ was identified uniquely on the basis of the systematic absences observed during the collection of data. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. The bridging hydride ligand was located and was successfully refined with an isotropic thermal parameter. All other hydrogen atom positions were calculated by assuming idealized geometries and employing observed atoms whenever possible. The contributions of these hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

Compound **3** crystallized in the monoclinic crystal system. The systematic absences observed during the data collection were consistent with either of the space groups $P2_1$ or $P2_1/m$. The space group $P2_1$ was originally chosen; however, due to difficulties in refinement the space group was changed to $P2_1/m$. The latter space group requires a crystallographic plane of symmetry to pass through the molecule and thus a 50/50 disorder of the methyl groups on the ethyl groups, but the refinement converged to yield excellent metrical parameters for the molecule in contrast to the space group $P2_1$. It is thus believed to be the correct space group. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. The bridging hydride ligand was located crystallographically and was successfully refined with an isotropic thermal parameter. All other hydrogen atom positions were calculated by assuming idealized geometries and employing observed atoms whenever possible. The contributions of these hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

Compound **4** crystallized in the monoclinic crystal system. The space group $P2_1/n$ was identified uniquely from the systematic absences observed during the collection of data. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. The two bridging hydride ligands were located crystallographically and their positions were refined with isotropic thermal parameters. All other hydrogen atom positions were calculated by assuming idealized geometries and employing observed atoms whenever possible. The contributions of these hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

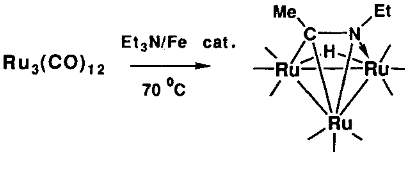
Table 3 Intramolecular distances[a] for **2**

Atom	Atom	Distance	Atom	Atom	Distance
Os(1)	C(12)	1.86(1)	Os(3)	H(1)	1.6(1)
Os(1)	C(13)	1.87(1)	Os(3)	C(31)	1.89(1)
Os(1)	C(11)	1.95(2)	Os(3)	C(33)	1.90(1)
Os(1)	C(2)	2.19(1)	Os(3)	C(32)	1.91(1)
Os(1)	Os(2)	2.9119(9)	Os(3)	N	2.149(9)
Os(1)	Os(3)	2.9257(8)	O	C(av.)	1.14(1)
Os(2)	C(24)	1.90(1)	N	C(1)	1.26(2)
Os(2)	C(22)	1.92(2)	N	C(3)	1.50(2)
Os(2)	C(21)	1.94(1)	C(1)	C(2)	1.49(2)
Os(2)	C(23)	1.96(1)	C(3)	C(4)	1.49(2)
Os(2)	Os(3)	2.8994(8)	Os(1)	H(1)	1.9(1)

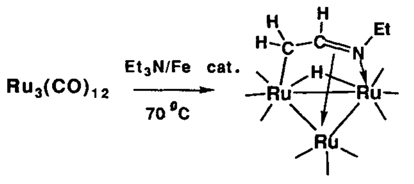
[a] Distances are in ångstrom units. Estimated standard deviations in the least significant figure are given in parentheses.

RESULTS AND DISCUSSION

As reported by Shapley, the dehydrogenation of triethylamine by the labile cluster complex $Os_3(CO)_{10}(NCMe)_2$ at 80 °C yields two products, $Os_3(CO)_{10}(\textit{anti}\text{-}\mu\text{-}\eta^1\text{-}CHCHNEt_2)(\mu\text{-}H)$ (**1**), 36 %, and $Os_3(CO)_{10}(\mu\text{-}H)_2$, 30 %.[22,23] However, the reaction also occurs at 25 °C to give compound **1** in 20 % yield. At this temperature $Os_3(CO)_{10}(\mu\text{-}H)_2$ is present only in trace amounts, and two new products **2** and **3** can be isolated in low yields, 4 % and 7 % respectively. Compounds **2** and **3** were characterized by IR, ^1H NMR and single-crystal X-ray diffraction analyses. Final atomic positional parameters are listed in Table 2. Selected interatomic distances and angles are listed in Tables 3 and 4, respectively. The molecular structure of **2** consists of a triangular cluster of three osmium atoms with ten linear carbonyl ligands arranged as shown in Fig. 1. The most interesting ligand is the $H_2CCHNEt$ group that bridges the Os(1)–Os(3) bond through the methylene carbon C(2) and the nitrogen atom: Os(1)–C(2) = 2.19(1) Å, Os(2)–N = 2.147(9) Å. The C(1)–N distance of 1.26(2) Å is indicative of a carbon–nitrogen double bond. The hydride ligand bridges the Os(1)–Os(3) bond ($\delta = -14.27$ ppm), and was located and refined crystallographically. The ligand in **2** is best viewed as a methyl-metallated μ–η^2-imine. It was evidently formed by the elimination of one of the ethyl groups of the NEt_3. Deeming *et al.* have reported the cleavage of a methyl group from NMe_3 by reaction with $Os_3(CO)_{12}$ at 170 °C to yield the complex $Os_3(CO)_{10}(\mu\text{-HC}{=}\text{NMe})(\mu\text{-H})$.[30] The cleavage of an ethyl group from NEt_3 by $Ru_3(CO)_{12}$ in the presence of a catalytic amount of $Fe_2(CO)_4(\mu\text{-SEt})_2(PPh_3)_2$ has also been reported (Eqns [9][31] and [10][32]).



[9]



[10]

The complex $Ru_3(CO)_9(\mu\text{-CH}_2\text{C(H)}{=}\text{NEt})(\mu\text{-H})$ was proposed to contain the same imine ligand as found in **2**, except that it was proposed to be coordinated in a triply bridging mode.[32]

An ORTEP diagram of the molecular structure of **3** is shown in Fig. 2. Final atomic positional parameters are listed in Table 5. Selected interatomic distances and bond angles are listed in Tables 6 and 7, respectively. Compound **3** is an isomer of compound **1** in which the $HCC(H)NEt_2$ ligand exhibits a *syn* conformation with respect to the metal triangle as opposed to the *anti* conformation found in **1**.[22,23] The molecule contains a crystallographically imposed mirror plane which passes through the atoms C(1), C(2), N, C(3), C(4), Os(2), C(21), O(21), C(23), O(23), and H. The methyl groups of the ethyl groups lie off the plane; thus each methyl group occupies two sites equally displaced from the plane due to disorder. We have chosen to represent a molecular conformation in Fig. 2 in which one methyl group lies on each side of the plane, but it is equally possible statistically that both methyl groups lie on the same side of the plane. The latter conformation was observed in the solid-state structure of **1**.[22,23] The dimensions of the $HCC(H)NEt_2$ ligand in **3** are similar to those found in **1** although the C(1)–C(2) distance of 1.32(2) Å in **3** is slightly

Table 4 Intramolecular bond angles[a] for **2**

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
C(12)	Os(1)	C(2)	84.9(5)	C(31)	Os(3)	N	173.6(5)
C(12)	Os(1)	Os(2)	175.4(4)	C(31)	Os(3)	Os(2)	88.3(3)
C(12)	Os(1)	Os(3)	116.4(4)	C(31)	Os(3)	Os(1)	92.4(4)
C(13)	Os(1)	C(2)	88.2(6)	C(33)	Os(3)	N	94.5(4)
C(13)	Os(1)	Os(2)	87.5(4)	C(33)	Os(3)	Os(2)	84.0(4)
C(13)	Os(1)	Os(3)	145.6(4)	C(33)	Os(3)	Os(1)	143.6(4)
C(11)	Os(1)	C(2)	174.3(5)	C(32)	Os(3)	N	87.4(4)
C(11)	Os(1)	Os(2)	91.8(4)	C(32)	Os(3)	Os(2)	178.1(3)
C(11)	Os(1)	Os(3)	94.8(4)	C(32)	Os(3)	Os(1)	119.6(4)
C(2)	Os(1)	Os(2)	92.2(3)	N	Os(3)	Os(2)	94.3(3)
C(2)	Os(1)	Os(3)	83.8(3)	N	Os(3)	Os(1)	83.9(3)
Os(2)	Os(1)	Os(3)	59.56(2)	Os(2)	Os(3)	Os(1)	59.98(2)
C(24)	Os(2)	Os(3)	157.8(4)	C(1)	N	C(3)	114(1)
C(24)	Os(2)	Os(1)	97.5(4)	C(1)	N	Os(3)	125.6(9)
C(22)	Os(2)	Os(3)	101.8(4)	C(3)	N	Os(3)	119.9(7)
C(22)	Os(2)	Os(1)	162.1(4)	N	C(1)	C(2)	127(1)
C(21)	Os(2)	Os(3)	86.3(4)	C(1)	C(2)	Os(1)	119.0(8)
C(21)	Os(2)	Os(1)	89.5(4)	C(4)	C(3)	N	112(1)
C(23)	Os(2)	Os(3)	90.3(3)	O	C(av.)	Os	177(1)
C(23)	Os(2)	Os(1)	87.8(4)	Os(1)	H(1)	Os(3)	111(1)
Os(3)	Os(2)	Os(1)	60.45(2)				

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

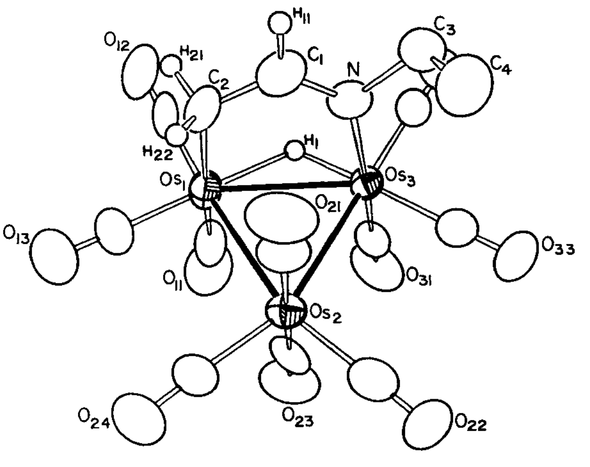


Figure 1 An ORTEP diagram of $Os_3(CO)_{10}[\mu\text{-}\eta^2\text{-}CH_2CH{=}NEt](\mu\text{-}H)$ (**2**) showing 50 %-probability thermal ellipsoids.

shorter than that in **1**, (1.42(3) Å). The C(2)–N distance of 1.32(2) Å, [1.28(2) Å for **1**] is indicative of partial multiple bonding character between these atoms. There is hindered rotation about the C(1)–N bond, as indicated by the observation of separate resonances for each of the methylene and methyl hydrogen atoms in the ^1H NMR spectrum. Compound **3** contains a hydride ligand (located and refined crystallographically, $\delta = -15.98$ ppm) that bridges the Os(1)–Os(1′) bond.

Compound **3** is thermally unstable and slowly isomerizes completely to **1** (Eqn [11]).

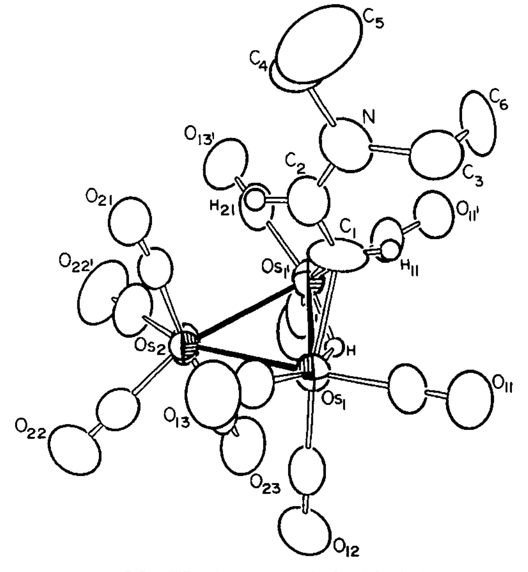
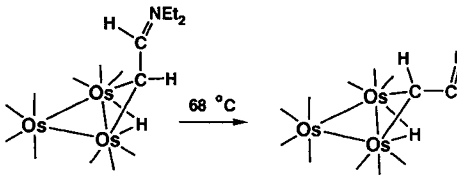
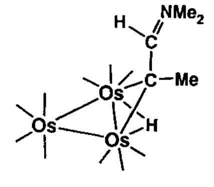


Figure 2 An ORTEP diagram of $Os_3(CO)_8(syn\text{-}\mu\text{-}CHCHNEt_2)(\mu\text{-}H)$ (**3**) showing 50 %-probability thermal ellipsoids.



[11]

The complex $Os_3(CO)_{10}[syn\text{-}\mu\text{-}CMeC(H){=}NMe_2](\mu\text{-}H)$ formed by insertion of MeC_2NMe_2 into a metal–hydrogen bond of $Os_3(CO)_{10}(\mu\text{-}H)_2$ exhibits a structure and $\mu\text{-}C(Me)CHNMe_2$ ligand conformation similar to that in **3**.[33]



$Os_3(CO)_{10}[\mu\text{-}CMeC(H){=}NMe_2](\mu\text{-}H)$

Compound **1** was found to undergo a facile photo-induced decarbonylation to yield two new compounds, **4** and **5**, in 58% and 21% yields, respectively. Both compounds were characterized by IR and ^1H NMR spectroscopy and by single-crystal X-ray diffraction analyses. Compound **5** was also prepared recently by the addition of NEt_2H to $Os_3(CO)_{10}(\mu_3\text{-}C{\equiv}CH)(\mu\text{-}H)$.[34] These workers also reported a structural characterization, and since their result is not significantly different from ours, we will not reproduce our results here.[25]

An ORTEP diagram of compound **4** is shown in Fig. 3. Final atomic positional parameters are listed in Table 8. Selected interatomic distances and bond angles are listed in Tables 9 and 10, respectively. The molecule consists of a triangular cluster of three osmium atoms with three linear carbonyl ligands on each metal atom. The most interesting ligand is the $\mu_3\text{-}CC(H)NEt_2$ ligand that caps one face of the metal triangle through the carbon atom C(1). The metal–C(1) distances are similar: Os(1)–C(1) = 2.12(1) Å; Os(2)–C(1) Å; and Os(3)–C(1) = 2.06(1) Å. The two hydride-bridged metal–metal bonds, Os(1)–Os(2) = 2.852 (1) Å and Os(1)–Os(3) = 2.864(1) Å, are significantly longer than the non-hydride-bridged bond, Os(2)–Os(3) = 2.7564(9) Å. Both hydride ligands were located crystallographically and their positions were successfully refined. In solution, the two hydride ligands are observed to be equivalent by the presence of a single resonance at $\delta = -19.31$ ppm. This is probably the result of a

Table 5 Positional parameters and B(eq) values for compound **3**

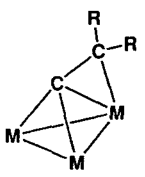
Atom	x	y	z	B(eq)
Os(1)	0.25429(06)	0.14024(04)	0.20773(04)	4.00(2)
Os(2)	0.59840(09)	1/4	0.29997(06)	4.44(3)
O(11)	−0.1163(12)	0.0323(07)	0.1046(08)	6.6(4)
O(12)	0.3100(14)	0.0200(10)	0.4378(10)	9.9(6)
O(13)	0.4682(13)	−0.0223(08)	0.1172(10)	7.9(5)
O(21)	0.6712(15)	1/4	0.0608(11)	5.4(6)
O(22)	0.8652(15)	0.0677(10)	0.3822(11)	10.0(7)
O(23)	0.488(02)	1/4	0.5268(13)	10(1)
N	0.125(02)	1/4	−0.1485(15)	8(1)
C(1)	0.165(03)	1/4	0.0559(14)	5.4(8)
C(2)	0.227(02)	1/4	−0.0368(18)	5.4(9)
C(3)	−0.077(04)	0.2051(17)	−0.189(02)	5(1)
C(4)	0.222(04)	0.279(02)	−0.238(02)	6(2)
C(5)	0.169(06)	0.199(03)	−0.329(04)	11(2)
C(6)	−0.197(04)	0.302(03)	−0.195(03)	8(2)
C(11)	0.0242(16)	0.0748(10)	0.1451(12)	5.1(6)
C(12)	0.2903(17)	0.0670(12)	0.3509(15)	6.8(7)
C(13)	0.3867(16)	0.0406(10)	0.1500(12)	5.3(6)
C(21)	0.633(02)	1/4	0.1455(16)	4.1(7)
C(22)	0.7631(19)	0.1346(12)	0.3506(13)	6.5(7)
C(23)	0.532(02)	1/4	0.4429(18)	6(1)
H	0.197(14)	1/4	0.252(10)	2.0
H(11)	0.0336	0.2500	0.0283	6.0
H(21)	0.3564	1/4	−0.0216	6.0

dynamic averaging process, but this was not confirmed by a variable-temperature NMR study. The alkenylidene hydrogen H(21) was not located in the structural analysis, but its location on C(2) was indicated by its characteristic low-field resonance ($\delta = 9.01$ ppm) in the ^{1}H NMR spectrum.[35] The position of H(21) shown in the figure was calculated by assuming idealized trigonal planar geometry. C(2) contains only three substituents. The short C(1)–(C2) and C(2)–N distances of 1.39(2) Å and 1.31(2) Å indicate a partial delocalization of the unsaturation along both of these bonds. The nitrogen atom has a planar geometry. The ethyl groups are inequivalent by ^{1}H NMR spectroscopy due to hindered rotation about the C(2)–N bond. The ligand can be formulated as a diethylamino-substituted vinylidene. Alkenylidene ligands in most polynuclear complexes adopt a μ_3–η^2 coordination mode with the ligand functioning as a four-electron donor, **A**.[36–38]

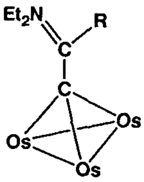
Table 6 Intramolecular distances[a] for **3**

Atom	Atom	Distance	Atom	Atom	Distance
Os(1)	Os(1′)	2.789(1)	Os(2)	C(23)	1.92(2)
Os(1)	Os(2)	2.8780(9)	O	C(av.)	1.15(2)
Os(1)	C(1)	2.22(1)	N	C(2)	1.32(2)
Os(1)	C(11)	1.88(1)	N	C(3)	1.58(3)
Os(1)	C(12)	1.89(2)	N	C(4)	1.53(3)
Os(1)	C(13)	1.88(1)	C(1)	C(2)	1.33(2)
Os(2)	C(21)	1.94(2)	C(3)	C(6)	1.52(3)
Os(2)	C(22)	1.91(2)	C(4)	C(5)	1.44(4)
Os(1)	H	1.60(1)			

[a] Distances are in ångstrom units. Estimated standard deviations in the least significant figure are given in parentheses.



A



B

In **3** the ligand has adopted an alternative μ_3–η^1 form, **B**. This may be due to the string interaction of the nitrogen lone pair with carbon C(2) which evidently supersedes and precludes bonding of the amine-substituted carbon atom to the metal atom. The formation of **4** probably occurs by a

Table 7 Intramolecular bond angles[a] for **3**

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
Os(1)	Os(1′)	Os(2)	61.01(2)	Os(1)	Os(2)	C(23)	83.0(4)
Os(1)	Os(1′)	C(1)	51.0(3)	Os(1′)	Os(2)	C(21)	90.9(4)
Os(1)	Os(1′)	C(11)	116.3(4)	Os(1′)	Os(2)	C(22)	158.5(4)
Os(1)	Os(1′)	C(12)	119.6(5)	Os(1′)	Os(2)	C(22)	100.6(4)
Os(1)	Os(1′)	C(13)	132.3(4)	Os(1′)	Os(2)	C(23)	83.0(4)
Os(2)	Os(1)	C(1)	91.1(5)	C(21)	Os(2)	C(22)	91.6(5)
Os(2)	Os(1)	C(11)	177.3(4)	C(21)	Os(2)	C(22)	91.6(5)
Os(2)	Os(1)	C(12)	91.9(4)	C(21)	Os(2)	C(23)	173.0(7)
Os(2)	Os(1)	C(13)	86.2(4)	C(22)	Os(2)	C(22)	100.7(9)
C(1)	Os(1)	C(11)	86.6(6)	C(22)	Os(2)	C(23)	92.8(5)
C(1)	Os(1)	C(12)	165.9(6)	C(2)	N	C(3)	122(2)
C(1)	Os(1)	C(13)	100.9(6)	C(2)	N	C(4)	116(2)
C(11)	Os(1)	C(12)	89.9(6)	C(3)	N	C(4)	110(2)
C(11)	Os(1)	C(13)	95.8(5)	Os(1)	C(1)	Os(1′)	77.9(5)
C(12)	Os(1)	C(13)	93.1(6)	Os(1′)	C(1)	C(2)	125(1)
Os(1)	Os(2)	Os(1′)	57.97(3)	N	C(2)	C(1)	126(2)
Os(1)	Os(2)	C(21)	90.9(4)	N	C(3)	C(6)	104(1)
Os(1)	Os(2)	C(22)	100.6(4)	N	C(4)	C(5)	105(2)
Os(1)	Os(2)	C(22)	158.5(4)	Os	C	O(av.)	177(1)

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

simple photo-induced decarbonylation of the $Os(CO)_4$ grouping in **1** to yield a vacant coordination site which then reacts with the C–H bond of the bridging carbon atom (Eqn [12]).

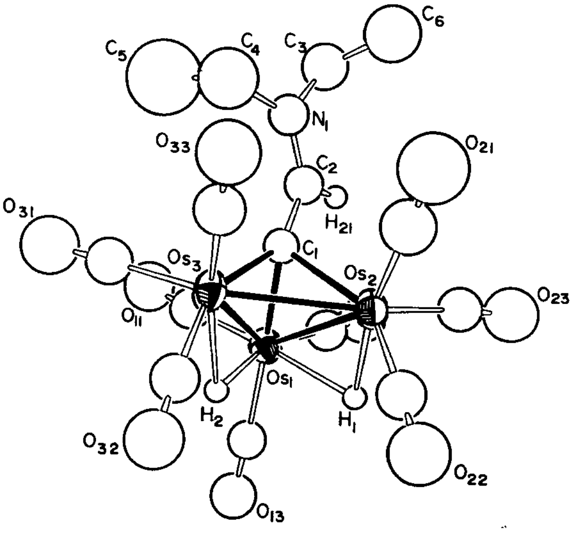
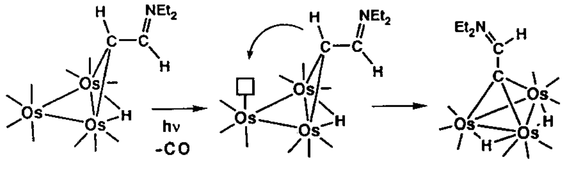
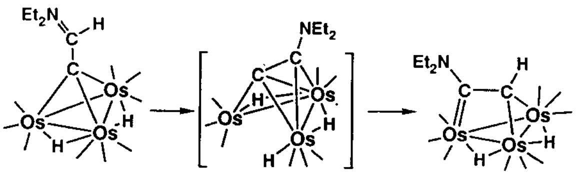


Figure 3 An ORTEP diagram of $Os_3(CO)_9(\mu_3\text{-}\eta^1\text{-}CC(H)NEt_2](\mu\text{-}H)_2$ (**4**) showing 50 %-probability thermal ellipsoids.



3 **4** [12]

Compound **4** undergoes a facile isomerization to **5** in 70 % yield in refluxing hexane. Overall, this transformation involves a 1,2 shift of the hydrogen atom from C(2) to C(1). Mechanistically, however, this may involve a metal-mediated C–H activation process with the formation of an intermediate, such as **C**, containing a μ-diethylaminoacetylide ligand and three



4 **C** **5**

Scheme 1

Table 8 Positional parameters and *B*(eq) values for compound **4**

Atom	*x*	*y*	*z*	*B*(eq)
Os(1)	0.56261(5)	0.20016(4)	0.74136(4)	3.13(2)
Os(2)	0.48519(5)	0.36998(4)	0.65738(4)	3.36(3)
Os(3)	0.57295(5)	0.36346(4)	0.84741(4)	3.29(3)
O(11)	0.512(1)	0.0814(9)	0.900(1)	7.5(3)
O(12)	0.389(1)	0.0885(8)	0.594(1)	7.1(3)
O(13)	0.828(1)	0.1173(7)	0.7213(9)	5.9(3)
O(21)	0.315(1)	0.533(1)	0.666(1)	9.8(4)
O(22)	0.707(1)	0.4790(8)	0.601(1)	7.5(3)
O(23)	0.354(1)	0.3090(9)	0.462(1)	7.9(3)
O(31)	0.587(1)	0.2806(9)	1.039(1)	8.0(3)
O(32)	0.847(1)	0.4520(8)	0.8737(9)	6.4(3)
O(33)	0.438(1)	0.5365(9)	0.883(1)	7.4(3)
N(1)	0.187(1)	0.2988(7)	0.799(1)	4.2(2)
C(1)	0.418(1)	0.2951(8)	0.767(1)	3.0(2)
C(2)	0.283(1)	0.275(1)	0.754(1)	4.0(3)
C(3)	0.051(2)	0.275(1)	0.763(1)	6.0(4)
C(4)	0.210(2)	0.349(2)	0.889(2)	8.5(6)
C(5)	0.219(3)	0.285(2)	0.962(3)	15(1)
C(6)	−0.016(2)	0.344(2)	0.701(2)	8.7(6)
C(11)	0.531(1)	0.125(1)	0.839(1)	5.1(3)
C(12)	0.457(1)	0.131(1)	0.652(1)	5.2(4)
C(13)	0.726(1)	0.148(1)	0.727(1)	4.2(3)
C(21)	0.382(2)	0.469(1)	0.663(1)	6.5(4)
C(22)	0.621(1)	0.438(1)	0.621(1)	5.0(3)
C(23)	0.399(1)	0.335(1)	0.539(1)	4.9(3)
C(31)	0.581(1)	0.314(1)	0.966(1)	5.0(3)
C(32)	0.742(1)	0.419(1)	0.866(1)	4.8(3)
C(33)	0.490(1)	0.469(1)	0.870(1)	5.2(4)
H(1)	0.60(1)	0.288(8)	0.64(1)	5(3)
H(2)	0.68(1)	0.251(9)	0.79(1)	6(3)

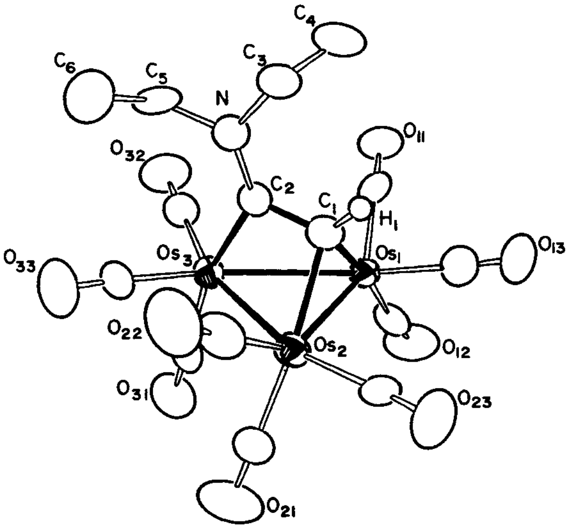


Figure 4 An ORTEP diagram of $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CHCNEt_2](\mu\text{-}H)_2$ (**5**) showing 50%-probability thermal ellipsoids.

hydride ligands, that subsequently shifts a hydride ligand to the acetylide carbon to yield **5** (Scheme 1). The reverse of this transformation (i.e. μ_3-alkyne to μ_3-alkenylidene) has been observed for cluster complexes containing terminal alkyne ligands.[37,39,40]

An ORTEP drawing of the molecular structure of compound **5** is shown in Fig. 4.[25] This molecule contains a triosmium cluster with a triply bridging HC_2NEt_2 ligand. This ligand is formally an 'ynamine', and it has adopted the well-known the μ_3-⊥-coordination mode **D** exhibited by alkynes,[41] but it differs from all other examples in that the amine-substituted carbon atom is coordinated to only one metal atom, **E**. This has been explained by the importance of the interaction of the lone pair of electrons on the nitrogen atom with the neighboring carbon atom.[42] As a result, the nitrogen atom exhibits a planar geometry. The C–N distance is short and indicative of multiple bonding between these atoms.[25] Also, the ethyl groups are inequivalent (by ^1H NMR spectroscopy) due to hindered rotation about the C(2)–N bond. These structural features are characteristic of metal-coordinated aminocarbene ligands[43,44] and suggest that a carbene-like character may exist at the amine-substituted carbon atom in **5** (see structure **E**). Accordingly, we propose that the ligand

Table 9 Intramolecular distances[a] for $Os_3(CO)_9[\mu_3\text{-}CC(H)\text{-}NEt_2](\mu\text{-}H)_2$, **4**

Atom	Atom	Distance	Atom	Atom	Distance
Os(1)	H(2)	1.7(1)	Os(3)	C(32)	1.89(1)
Os(1)	H(1)	2.1(1)	Os(3)	C(1)	2.06(1)
Os(1)	C(12)	1.85(2)	O(11)	C(11)	1.14(2)
Os(1)	C(11)	1.88(2)	O(12)	C(12)	1.17(2)
Os(1)	C(13)	1.88(1)	O(13)	C(13)	1.16(1)
Os(1)	C(1)	2.12(1)	O(21)	C(21)	1.17(2)
Os(1)	Os(2)	2.852(1)	O(22)	C(22)	1.15(2)
Os(1)	Os(3)	2.864(1)	O(23)	C(23)	1.19(2)
Os(2)	H(1)	1.9(1)	O(31)	C(31)	1.17(2)
Os(2)	C(21)	1.82(2)	O(32)	C(32)	1.16(2)
Os(2)	C(22)	1.87(2)	O(33)	C(33)	1.16(2)
Os(2)	C(23)	1.87(2)	N(1)	C(2)	1.31(2)
Os(2)	C(1)	2.15(1)	N(1)	C(3)	1.44(2)
Os(2)	Os(3)	2.7563(9)	N(1)	C(4)	1.49(3)
Os(3)	H(2)	2.2(1)	C(1)	C(2)	1.39(2)
Os(3)	C(33)	1.84(2)	C(3)	C(6)	1.46(3)
Os(3)	C(31)	1.86(2)	C(4)	C(5)	1.40(4)

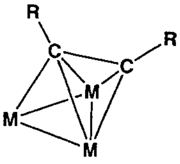
[a] Distances are in ångstrom units. Estimated standard deviations in the least significant figure are given in parentheses.

Table 10 Intramolecular bond angles[a] for $Os_3(CO)_9[\mu_3\text{-}CC(H)NEt_2](\mu\text{-}H)_2$, **4**

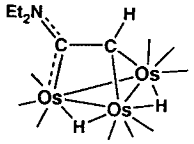
Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
C(12)	Os(1)	C(11)	92.3(7)	Os(3)	Os(2)	Os(1)	61.38(2)
C(12)	Os(1)	C(13)	96.7(6)	C(33)	Os(3)	C(31)	96.7(7)
C(12)	Os(1)	C(1)	99.0(6)	C(33)	Os(3)	C(32)	92.2(6)
C(12)	Os(1)	Os(2)	96.2(5)	C(33)	Os(3)	C(1)	100.8(6)
C(12)	Os(1)	Os(3)	144.3(5)	C(33)	Os(3)	Os(2)	93.9(6)
C(11)	Os(1)	C(13)	96.3(6)	C(33)	Os(3)	Os(1)	147.3(5)
C(11)	Os(1)	C(1)	92.6(6)	C(31)	Os(3)	C(32)	98.5(7)
C(11)	Os(1)	Os(2)	141.2(5)	C(31)	Os(3)	C(1)	103.6(6)
C(11)	Os(1)	Os(3)	95.4(5)	C(31)	Os(3)	Os(2)	153.7(5)
C(13)	Os(1)	C(1)	161.5(5)	C(31)	Os(3)	Os(1)	99.1(5)
C(13)	Os(1)	Os(2)	120.0(4)	C(32)	Os(3)	C(1)	152.7(6)
C(13)	Os(1)	Os(3)	116.9(4)	C(32)	Os(3)	Os(2)	105.1(5)
C(1)	Os(1)	Os(2)	48.6(4)	C(32)	Os(3)	Os(1)	113.3(5)
C(1)	Os(1)	Os(3)	45.9(3)	C(1)	Os(3)	Os(2)	50.6(4)
Os(2)	Os(1)	Os(3)	57.67(2)	C(1)	Os(3)	Os(1)	47.6(3)
C(21)	Os(2)	C(22)	92.3(7)	Os(2)	Os(3)	Os(1)	60.95(2)
C(21)	Os(2)	C(23)	94.8(8)	C(2)	N(1)	C(3)	121(1)
C(21)	Os(2)	C(1)	97.0(7)	C(2)	N(1)	C(4)	123(1)
C(21)	Os(2)	Os(3)	94.3(6)	C(3)	N(1)	C(4)	115(1)
C(21)	Os(2)	Os(1)	144.6(6)	C(2)	C(1)	Os(3)	146(1)
C(22)	Os(2)	C(23)	98.6(7)	C(2)	C(1)	Os(1)	123(1)
C(22)	Os(2)	C(1)	146.6(6)	C(2)	C(1)	Os(2)	116(1)
C(22)	Os(2)	Os(3)	99.8(5)	Os(3)	C(1)	Os(1)	86.4(4)
C(22)	Os(2)	Os(1)	115.7(5)	Os(3)	C(1)	Os(2)	81.7(4)
C(23)	Os(2)	C(1)	112.4(6)	Os(1)	C(1)	Os(2)	83.7(4)
C(23)	Os(2)	Os(3)	159.1(5)	N(1)	C(2)	C(1)	133(1)
C(23)	Os(2)	Os(1)	101.5(5)	N(1)	C(3)	C(6)	112(1)
C(1)	Os(2)	Os(3)	47.7(3)	C(5)	C(4)	N1	108(2)
C(1)	Os(2)	Os(1)	47.6(3)	O	C	Os(av.)	177(2)

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

in **5** can be described alternatively as a dimetallated methyl(diethylamino)carbene ligand.[25] Similar formulations have been made for coordinated ynamines in other cluster complexes.[45–47] The molecule also contains two hydride ligands which are observed as broad singlets ($\delta = -16.35$ and -18.90 ppm) in the ^1H NMR spectrum. At 102 °C these resonances have coalesced to a singlet at $\delta = -18.15$ ppm due to dynamic averaging. These ligands are believed to bridge the two elongated metal–metal bonds, Os(1)–Os(2) = 2.832(1) Å and Os(1)–Os(3) = 3.003(1) Å.[12]

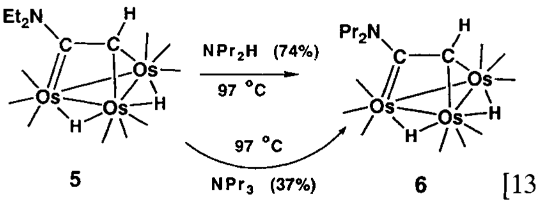


D



E

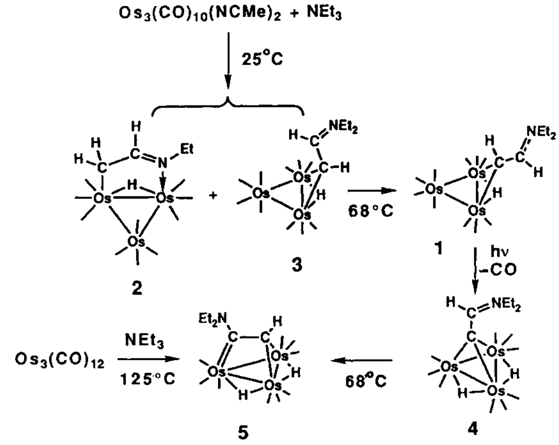
The formulation of carbene character in the ynamine ligand is also supported by its reactivity.[43,44] For example, the amino group of the HC_2NEt_2 ligand is readily exchanged by reaction with secondary amines. The reaction of **5** with NPr_2H at 97 °C yielded the derivative $Os_3(CO)_9(\mu_3\text{-}HC_2NPr^n_2)(\mu\text{-}H)_2$ (**6**) in 74 % yield (Eqn [13]).



[13]

We have subsequently found that **5** can also be obtained in 25 % yield directly from the reaction of $Os_3(CO)_{12}$ with NEt_3 in refluxing octane. It thus occurred to us that compound **5** could have been formed in the catalytic transalkylation reaction between NEt_3 and NPr_3 using $Os_3(CO)_{12}$ that was reported by Laine.[10–14] We found that compound **6** is also obtained in 37 % yield from the reaction of **5** with NPr_3 at 97 °C, and solutions of compound **5** also produce exchange of the alkyl groups between NEt_3 and NPr_3 catalytically at 125 °C; however, at this temperature there is a substantial amount of decomposition of **5** and a detailed analysis of the catalyst was therefore not possible (Adams, R D and Tanner, J T, unpublished results).

The results of our study of the reactions of $Os_3(CO)_{12}$ with NEt_3 are summarized in Scheme 2.



Scheme 2

This sequence of reactions has demonstrated new features of the stepwise process of the removal of hydrogen atoms from triethylamine to yield the dimetallated methyl(diethylamino)carbene complex, **5**. We have also shown that complex **5** engages in some very unusual transformations that involve carbon–nitrogen bond cleavage and could be an active species for catalytic processes such as the metathesis of alkyl groups between tertiary amines. These results provide further confirmation of the general principle that multicenter coordination can produce novel ligand reactivity.[49–51]

SUPPLEMENTARY MATERIAL AVAILABLE

Tables of anisotropic thermal parameters and structure factor amplitudes (47 pages) for all three structural analyses are available upon request from RDA.

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