Reversible Carbon–Nitrogen Bond Formation in the Isomerisation of Triosmium Compounds derived from t-Butyldiazomethane (Bu^tCHN_2); the *X*-Ray Crystal Structure of [$Os_3H_2(Bu^tCH{=}NNCO)(CO)_8(PMe_2Ph)$] †

Antony J. Deeming,* Yoshio Fuchita, and Kenneth Hardcastle
Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ
Kim Henrick and Mary McPartlin
Department of Chemistry, The Polytechnic of North London, Holloway, London N7 8DB

The dihydride [$Os_3H_2(CO)_{10}$] reacts with the diazoalkane Bu^tCHN_2 to give [$Os_3H(Bu^tCH{=}NNH)(CO)_{10}$] in the same way as reported for other diazoalkanes. A compound believed to be [$Os_3(\mu\text{-}CH_2Bu^t)(\mu\text{-}Bu^tCH{=}NNH)(CO)_{10}$] is also formed. However, [$Os_3H_2(CO)_9(PMe_2Ph)$] reacts with Bu^tCHN_2 to give a good yield of a novel type of compound [$Os_3H_2(Bu^tCH{=}NNCO)(CO)_8(PMe_2Ph)$] (*X*-ray structure reported). Instead of Bu^tCHN_2 addition being followed by insertion into an Os–H bond, the Bu^tCHN_2 molecule couples with CO to give the μ_3-isocyanate ligand RNCO (R = $Bu^tCH{=}N$) bonded to the Os_3 triangle through N and C atoms. Protonation with CF_3CO_2H leads by C–N cleavage to [$Os_3H_2(Bu^tCH{=}NNH)(CO)_9(PMe_2Ph)$]$^+$. On deprotonation of this cation, the C–N bond reforms to regenerate the $Bu^tCH{=}NNCO$ compound, but the isomer [$Os_3H(Bu^tCH{=}NNH)(CO)_9(PMe_2Ph)$] is also formed. This monohydride isomerises thermally to an isomer with the same formulation that is also formed by thermal substitution of [$Os_3H(Bu^tCH{=}NNH)(CO)_{10}$]. In all, three isomers have been identified, two differing in the positions of PMe_2Ph substitution which are clearly established by J_{PH} values for the hydrido-ligands.

Several reports have appeared on reactions between [$Os_3H_2(CO)_{10}$] with diazoalkanes R_2CN_2. Only in the case of CH_2N_2 does displacement of N_2 occur to give an alkyl cluster [$Os_3H(Me)(CO)_{10}$] which is in equilibrium with [$Os_3H_2(CH_2)(CO)_{10}$].[1,2] Attempts to obtain bridging alkyl or alkylidene clusters by this route from other diazoalkanes $R^1R^2CN_2$ all led to insertion without N_2 elimination to give [$Os_3H(R^1R^2C{=}NNH)(CO)_{10}$].[3,4] Two compounds have had *X*-ray structures determined: [$Os_3H(Ph_2C{=}NNH)(CO)_{10}$],[3,4] and [$Os_3H(PhMeC{=}NNH)(CO)_{10}$].[3] These are members of a large class of compounds, including [$Os_3H(PhNH)(CO)_{10}$],[5,6] having amido-ligands bridging through one of the nitrogen atoms. Hoping that Bu^tCHN_2 for steric reasons might just behave like CH_2N_2 rather than other diazoalkanes, we treated it with [$Os_3H_2(CO)_{10}$] in an attempt to obtain [$Os_3H(CH_2Bu^t)(CO)_{10}$] or [$Os_3H_2(CHBu^t)(CO)_{10}$]. We had plans to explore the possibility of γ-elimination leading to [$Os_3H_2(CH_2CMe_2CH_2)(CO)_{10}$]. However, Bu^tCHN_2 does react like most other diazoalkanes and gives [$Os_3H(Bu^tCH{=}NNH)(CO)_{10}$]. Substitution by tertiary phosphines sometimes changes the course of reactions drastically, so we subsequently treated Bu^tCHN_2 with [$Os_3H_2(CO)_9(PMe_2Ph)$]. Although N_2 was not eliminated, a novel kind of compound was obtained, isomeric with [$Os_3H(Bu^tCH{=}NNH)(CO)_9(PMe_2Ph)$], but containing a μ_3 ligand derived by coupling Bu^tCHN_2 and CO. This N–C coupling reaction and the reverse N–C cleavage are the subjects of this paper.

Results and Discussion

Reactions of Bu^tCHN_2 *with Triosmium Dihydride Clusters.*—The compound Bu^tCHN_2 was prepared[7] by heating Li[$4\text{-}MeC_6H_4SO_2NN{=}CHBu^t$] and reacted at below 5 °C with [$Os_3H_2(CO)_{10}$] to give the cluster [$Os_3H(Bu^tCH{=}NNH)(CO)_{10}$] (1), in 23% yield, characterised by elemental analysis, ^1H n.m.r. and i.r. spectroscopy (Table 1 and Experimental section). The spectra for compound (1) correspond directly with those for compounds such as [$Os_3H(Ph_2C{=}NNH)(CO)_{10}$][3,4] and there can be no doubt that (1) has the structure shown in Scheme 1. In particular the hydride ^1H n.m.r. signal is a doublet (J_{HH} 2.5 Hz) characteristic of compounds of type [$Os_3H(RNH)(CO)_{10}$]. A low yield (9%) of another compound which we formulate tentatively as [$Os_3(\mu\text{-}CH_2Bu^t)(\mu\text{-}Bu^tCH{=}NNH)(CO)_{10}$] (2), was also obtained. It is clear from elemental analysis that two Bu^tCHN_2 molecules have been incorporated with the loss of one N_2 molecule. One set of ^1H n.m.r. signals seems to correspond with the $Bu^tCH{=}NNH$ ligand while the remaining AB quartet (δ 3.32 and 2.42, J_{HH} 17.8 Hz) and singlet (δ 1.03) to a CH_2Bu^t group, hence the formulation given. However, if the $Bu^tCH{=}NNH$ ligand is bound as in compound (1), there is no reason for the CH_2 protons to be diastereotopic. Possibly this ligand is bonded unsymmetrically as shown but without the good single crystals necessary for an *X*-ray structure we cannot be certain of the structure of (2). As formulated there is no need for agostic bonding in the μ-CH_2Bu^t group. This ligand (as a radical) is formally a one-electron donor and the CH_2 signals in the ^1H n.m.r. spectrum are at relatively low field as expected for this situation.

The formation of cluster (1) from Bu^tCHN_2 and [$Os_3H_2(CO)_{10}$] is unremarkable; other diazo compounds react similarly.[3,4] However, since [$Os_3H_2(CO)_9(PMe_2Ph)$] is known to behave differently from its parent in various reactions (see ref. 8 for examples), this dihydride was also treated with Bu^tCHN_2

[†] 1,1,2,2,2,3,3,3-Octacarbonyl-μ_3-[5′,5′-dimethyl-1′-oxo-2′,3′-diazahex-3′-ene-1′,2′-diyl-$C^{1'}(Os^2)N^{2'}(Os^{1,3})$]-1-dimethylphenylphosphine-1,2;1,3-di-μ-hydrido-*triangulo*-triosmium.

Supplementary data available (No. SUP 56608, 6 pp.): thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

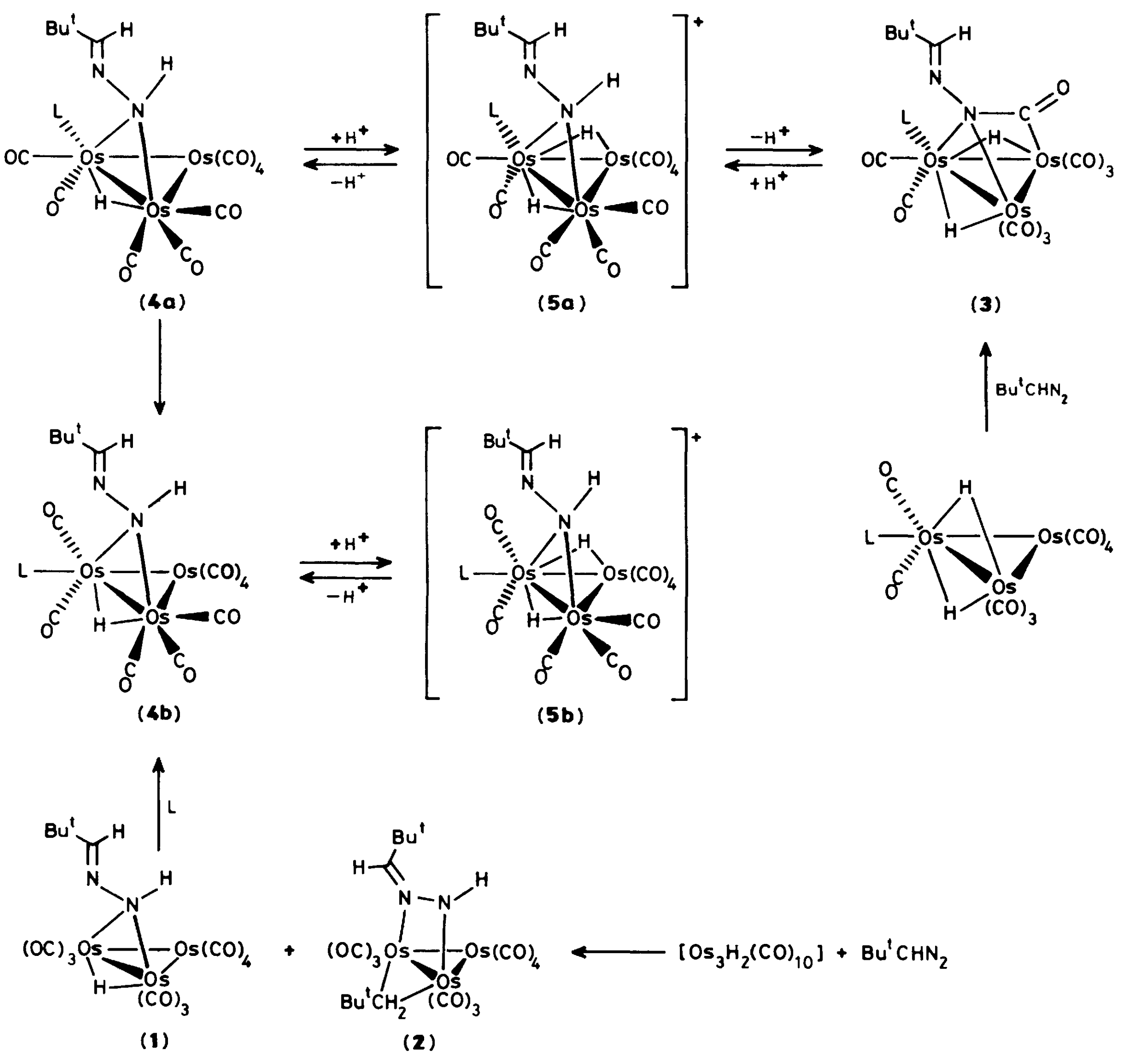
Table 1. Proton n.m.r. and i.r. data for the new compounds

Compound	$\tilde{\nu}$(CO)[a]/cm^{-1}	^{1}H N.m.r.[b]	
(1) [$Os_3H(Bu^tCH{=}NNH)(CO)_{10}$]	2 102w, 2 066vs, 2 051s, 2 017vs, 1 998vs, 1 980w, 1 973w	7.01 (s)	CH, NH[c]
		1.04 (s)	Bu^t
		−14.64 (d)	OsH, J_{HH} 2.5
(2) [$Os_3(CH_2Bu^t)(Bu^tCH{=}NNH)(CO)_{10}$]	2 096w, 2 064vs, 2 043s, 2 005vs, 1 999s, 1 990m, 1 984m, 1 973m, 1 964w	6.75 (s)	NH
		5.36 (s)	CH
		3.32 (d)	CH$_2$, J_{HH} 17.8
		2.42 (d)	
		1.04 (s)	Bu^t
		1.03 (s)	Bu^t
(3) [$Os_3H_2(Bu^tCH{=}NNCO)(CO)_8(PMe_2Ph)$]	2 084m, 2 049vs, 2 045s, 2 006vs, 1 993m, 1 983m, 1 974m, 1 669vw	7.45—7.65	Ph
		6.68 (s)	CH
		2.22 (d)	PMe, J_{PH} 10.8
		2.09 (d)	PMe, J_{PH} 10.8
	[d]2 081s, 2 043s, 2 004s, 1 994s, 1 978s, 1 961s, 1 638s	1.11 (s)	Bu^t
		−15.38 (d)	OsH, J_{PH} 28.9
		−17.76 (d)	OsH, J_{PH} 11.6
(4a) [$Os_3H(Bu^tCH{=}NNH)(CO)_9(PMe_2Ph)$]	2 083m, 2 044s, 2 008vs, 2 001m, 1 998m, 1 965m, 1 954m	7.35—7.50	Ph
		6.67 (s)	CH
		6.60 (s, br)	NH
		2.21 (d)	PMe, J_{PH} 9.3
		2.16 (d)	PMe, J_{PH} 9.3
		1.01 (s)	Bu^t
		−14.37 (dd)	OsH, J_{PH} 29.9, J_{HH} 2.3
(4b) [$Os_3H(Bu^tCH{=}NNH)(CO)_9(PMe_2Ph)$]	2 084m, 2 045vs, 2 006vs, 1 989m, 1 980m, 1 996m, 1 955w, 1 946w	7.40—7.65	Ph
		7.35 (s)	NH
		7.03 (s)	CH
		2.21 (d)	PMe, J_{PH} 1.0.
		2.07 (d)	PMe, J_{PH} 10.0
		0.91 (s)	Bu^t
		−14.26 (dd)	OsH, J_{PH} 8.3, J_{HH} 2.9
(5a) [$Os_3H_2(Bu^tCH{=}NNH)(CO)_9(PMe_2Ph)$]	*e*	7.40—7.65	Ph
		6.85 (s)	CH
		f	NH
		2.41 (d)	PMe, J_{PH} 10.7
		2.32 (s)	PMe, J_{PH} 10.7
		1.05 (s)	Bu^t
		−14.05 (d)	OsH, J_{PH} 26.4, J_{HH} 1.6
		−18.00 (d)	OsH, J_{PH} 13.8
(5b) [$Os_3H_2(Bu^tCH{=}NNH)(CO)_9(PMe_2Ph)$]$^+$	*e*	7.40—7.65	Ph
		7.27 (s)	CH + NH
		2.47 (d)	PMe, J_{PH} 11.0
		2.22 (d)	PMe, J_{PH} 11.0
		1.07 (s)	Bu^t
		−14.13 (dd)	OsH, J_{PH} 9.7, J_{HH} 2.0
		−17.80 (d)	OsH, J_{PH} 20.7

[a] In cyclohexane. [b] In $CDCl_3$; cations in $CDCl_3$ with added CF_3CO_2H. [c] δ 7.65 (s), NH; 7.44 (s), CH in $(CD_3)_2CO$. [d] In Nujol. [e] Not isolated. [f] Not assigned.

and gave a moderate yield (62%) of [$Os_3H_2(Bu^tCH{=}NNCO)(CO)_8(PMe_2Ph)$] (**3**). Although this has the same molecular formula as [$Os_3H(Bu^tCH{=}NNH)(CO)_9(PMe_2Ph)$] which would be the product corresponding to compound (**1**), it is clear that (**3**) is a dihydride (^{1}H n.m.r. doublets at δ −15.38 and −17.76). Furthermore a CO absorption at 1 669 cm^{-1} (cyclohexane solution) suggested an unusual ligand formulation. These results justified a single-crystal *X*-ray structure determination.

Structure of [$Os_3H_2(Bu^tCH{=}NNCO)(CO)_8(PMe_2Ph)$], *Cluster* (**3**).—Table 2 contains fractional atomic co-ordinates for compound (**3**) and Tables 3 and 4 selected bond lengths and angles respectively. The Os_3 cluster contains a novel μ_3-$Bu^tCH{=}NNCO$ ligand, two edge-bridging hydrido ligands as well as eight terminal CO and a PMe_2Ph ligand (Figure). One axial CO ligand of the $Os(CO)_4$ group of [$Os_3H_2(CO)_9(PMe_2Ph)$] has coupled with the terminal N atom of the incoming Bu^tCHN_2 molecule to give a four-electron-donating μ_3-isocyanate ligand. Although not previously demonstrated, other RNCO molecules could, in principle, bridge in this way. 4-Tolyl isocyanate ($4\text{-}MeC_6H_4NCO$) has been shown to react with [$Os_3H_2(CO)_{10}$] to give [$Os_3H(4\text{-}MeC_6H_4NCHO)(CO)_{10}$],[8] but with one less CO ligand present, the analogue of (**3**), [$Os_3H_2(4\text{-}MeC_6H_4NCO)(CO)_9$], might be expected. The geometry of the $Bu^tCH{=}NNCO$ shows no unexpected features and the $Bu^tCH{=}N$ group relates to the $Ph_2C{=}N$ and $PhMeC{=}N$ groups found in the clusters [$Os_3H(R^1R^2C{=}NNH)(CO)_{10}$].[3,4] The carbon atom C(23) of the carbonyl group of the μ_3 ligand has distorted trigonal planar geometry [N(1)–C(23)–O(23) 121, O(23)–C(23)–Os(2) 135, and N(1)–C(23)–Os(2) 104°] and the N(1)–C(23) distance of 1.46(2) Å indicates an essentially single bond consistent with the representation of (**3**) in the Schemes. Multiple bonding in the N(1)–C(23) interaction as commonly found in amide linkages is largely eliminated by there being four-co-ordination at N(1). The N(1)–N(2) bond length [1.468(17) Å] is close to the value expected (1.44 Å) for a single bond.



Scheme 1. L = PMe_2Ph

Table 2. Fractional atomic co-ordinates for $[Os_3H_2(Bu^tCH{=}NNCO)(CO)_8(PMe_2Ph)]$ (3)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	0.169 32(2)	0.429 85(5)	−0.031 21(7)	O(33)	0.222 0(6)	0.104 7(13)	−0.210 6(17)
Os(2)	0.147 25(2)	0.343 26(6)	0.240 58(7)	N(1)	0.117 3(4)	0.286 5(10)	−0.030 9(12)
Os(3)	0.188 48(2)	0.203 52(6)	0.050 61(8)	N(2)	0.086 6(4)	0.254 7(12)	−0.157 6(14)
C(11)	0.224 5(5)	0.539 1(14)	−0.008 7(18)	C(1)	0.064 7(6)	0.154 9(16)	−0.157 0(22)
O(11)	0.257 1(4)	0.603 6(10)	0.012 7(14)	C(2)	0.030 5(6)	0.114 4(20)	−0.279 2(23)
C(12)	0.177 6(5)	0.412 5(14)	−0.214 6(22)	C(3)	0.021 1(8)	0.211 4(20)	−0.394 2(26)
O(12)	0.181 6(5)	0.401 1(13)	−0.331 1(14)	C(4)	−0.022 2(7)	0.073 4(25)	−0.229 3(29)
C(21)	0.213 0(6)	0.372 4(14)	0.350 2(19)	C(5)	0.058 9(8)	0.010 0(19)	−0.332 2(24)
O(21)	0.251 7(4)	0.389 1(11)	0.414 2(14)	P	0.104 5(1)	0.570 5(3)	−0.086 7(4)
C(22)	0.131 0(7)	0.216 6(19)	0.338 1(20)	C(101)	0.124 9(5)	0.673 4(13)	−0.208 0(20)
O(22)	0.121 4(5)	0.137 0(14)	0.402 5(15)	C(102)	0.160 6(6)	0.758 3(15)	−0.160 4(23)
C(23)	0.088 6(5)	0.300 9(14)	0.087 5(16)	C(103)	0.182 2(9)	0.832 9(21)	−0.252 5(36)
O(23)	0.042 0(3)	0.280 8(10)	0.082 2(12)	C(104)	0.163 9(9)	0.821 6(22)	−0.391 3(36)
C(24)	0.102 6(6)	0.442 9(18)	0.326 0(19)	C(105)	0.128 4(9)	0.737 9(22)	−0.443 1(25)
O(24)	0.074 7(5)	0.499 4(14)	0.381 1(15)	C(106)	0.108 9(7)	0.662 5(17)	−0.348 2(20)
C(31)	0.253 4(7)	0.175 9(15)	0.152 0(19)	C(107)	0.086 9(6)	0.654 7(15)	0.052 9(18)
O(31)	0.293 6(5)	0.164 4(11)	0.216 4(15)	C(108)	0.041 7(5)	0.512 4(13)	−0.161 3(17)
C(32)	0.157 7(6)	0.069 3(14)	0.109 3(22)	H(1)	0.231(4)	0.330(9)	0.023(12)
O(32)	0.141 8(5)	−0.015 0(12)	0.145 8(18)	H(2)	0.149(4)	0.452(10)	0.129(12)
C(33)	0.210 2(6)	0.138 9(17)	−0.114 6(22)				

Table 3. Selected bond lengths (Å) for $[Os_3H_2(Bu^tCH{=}NNCO)(CO)_8(PMe_2Ph)]$ (**3**)

Os(1)–Os(2)	3.002(1)	Os(1)–Os(3)	2.810(1)
Os(1)–C(11)	1.900(15)	Os(1)–C(12)	1.874(22)
Os(1)–N(1)	2.142(11)	Os(1)–P	2.363(4)
Os(2)–Os(3)	2.791(1)	Os(2)–C(21)	1.939(16)
Os(2)–C(22)	1.885(22)	Os(2)–C(23)	2.087(14)
Os(2)–C(24)	1.893(19)	Os(3)–C(31)	1.879(18)
Os(3)–C(32)	1.880(17)	Os(3)–C(33)	1.945(22)
Os(3)–N(1)	2.146(10)	C(23)–O(23)	1.207(17)
C(23)–N(1)	1.460(20)	N(1)–N(2)	1.468(17)
N(2)–C(1)	1.299(23)	C(1)–C(2)	1.50(3)
C(2)–C(3)	1.62(3)	C(2)–C(4)	1.56(3)
C(2)–C(5)	1.54(3)	P–C(101)	1.823(18)
P–C(107)	1.801(19)	P–C(108)	1.828(13)

Average C–C (aryl) 1.41(1), average C–O (carbonyl) 1.14(2)

Table 4. Selected bond angles (°) for $[Os_3H_2(Bu^tCH{=}NNCO)(CO)_8(PMe_2Ph)]$ (**3**)

Os(3)–Os(1)–Os(2)	57.3(1)	C(11)–Os(1)–Os(2)	109.0(5)
C(11)–Os(1)–Os(3)	120.0(5)	N(1)–Os(1)–Os(2)	64.0(3)
C(12)–Os(1)–Os(3)	98.5(5)	N(1)–Os(1)–Os(3)	49.1(3)
P–Os(1)–Os(2)	105.0(1)	P–Os(1)–Os(3)	145.8(1)
P–Os(1)–N(1)	97.6(3)	C(21)–Os(2)–Os(1)	102.7(5)
C(22)–Os(2)–Os(3)	89.3(6)	Os(3)–Os(2)–Os(1)	57.9(1)
C(23)–Os(2)–Os(1)	66.7(4)	C(21)–Os(2)–Os(3)	97.1(3)
C(24)–Os(2)–Os(1)	111.9(6)	C(23)–Os(2)–Os(3)	69.7(4)
N(1)–Os(3)–Os(1)	49.0(3)	Os(2)–Os(3)–Os(1)	64.8(1)
C(31)–Os(3)–Os(1)	116.0(5)	C(31)–Os(3)–Os(2)	96.1(6)
N(1)–Os(3)–Os(2)	68.2(3)	C(32)–Os(3)–Os(2)	94.9(6)
C(33)–Os(3)–Os(2)	164.5(6)	C(33)–Os(3)–Os(1)	100.3(6)
O(23)–C(23)–Os(2)	135(1)	N(1)–C(23)–O(23)	121(1)
N(1)–C(23)–Os(2)	103.9(8)	C(23)–N(1)–Os(1)	105.6(9)
Os(3)–N(1)–Os(1)	81.9(3)	N(2)–N(1)–Os(1)	118.4(9)
C(23)–N(1)–Os(3)	102.6(8)	N(2)–N(1)–C(23)	117(1)
N(2)–N(1)–Os(3)	124.7(9)	C(2)–C(1)–N(2)	120(2)
C(1)–N(2)–N(1)	115(1)		

Average Os–C–O 177(1)

The hydrido-ligands were unambiguously located along the Os(1)–Os(3) and Os(1)–Os(2) edges (see Experimental section) and, as expected, they are bonded to the most electron-rich (PMe_2Ph-substituted) osmium atom. The ^1H n.m.r. signal at δ −15.38 with a large J_{PH} value (28.9 Hz) is then assigned to the hydride bridging Os(1) and Os(3) which is *trans* to the phosphine ligand. The other hydride between Os(1) and Os(2) is *cis* to the phosphine and gives a much smaller coupling; J_{PH} = 11.6 Hz. The values of J_{PH} may be used to assign tertiary phosphine co-ordination sites in this way.

Scheme 2 shows how we believe that cluster (**3**) is formed. The addition of Bu^tCHN_2 would give an adduct $[Os_3H_2(CO)_9L(Bu^tCHN_2)]$ (L = CO or PMe_2Ph) which contains a very nucleophilic osmium-bonded nitrogen atom and possibly has the structure shown although others are possible. When L = CO, proton transfer from osmium to this nitrogen atom would lead to cluster (**1**). When L = PMe_2Ph, proton transfer would be much less favourable since the metal centres would be more basic and the hydride ligands correspondingly less acidic. Under these conditions attack of the nucleophilic nitrogen atom at an axial CO of the $Os(CO)_4$ group leads to cluster (**3**). Clusters (**1**) and (**3**) are thermally robust and do not change in refluxing heptane (98 °C) over many hours. Probably these are the thermodynamically most stable forms in each case. However, we propose that the N–C bond formation leading the cluster (**3**) is reversible because protonation leads to the cation expected from protonation of the nucleophilic nitrogen atom of the intermediate shown in Scheme 2 (see next section).

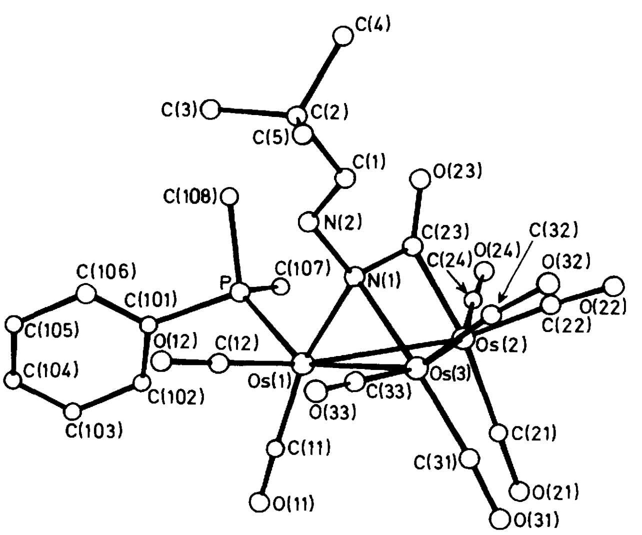
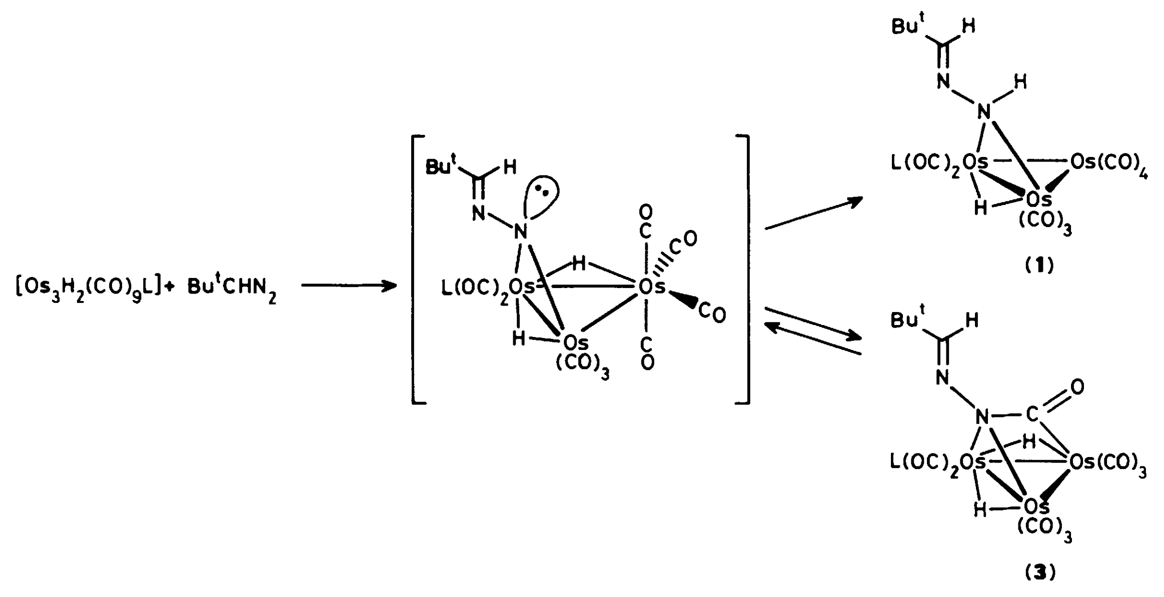


Figure. Molecular structure of $[Os_3H_2(Bu^tCH{=}NNCO)(CO)_8(PMe_2Ph)]$ (**3**). Hydrogen atoms were not located except the metal hydride ligands which bridge Os(1)–Os(3) and Os(1)–Os(2) (see Experimental section). No hydrogen atoms are shown

Coupling of CO and diazoalkane has also been reported for the reaction of CH_2N_2 with $[Mn_2(CO)_5(dppm)_2]$ (dppm = $Ph_2PCH_2PPh_2$) but in this case C–C rather than N–C coupling occurs to give $[Mn_2(NNCH_2CO)(CO)_4(dppm)_2]$.[9] Although N–C coupling in reactions of diazoalkanes with metal carbonyls has not previously been reported, the reaction of $[Os_3(CO)_{11}L]$ [L = MeCN or pyridine (py)] with phenyl azide (PhN_3) gives $[Os_3(CO)_{10}L(PhN_3CO)]$.[10] The weakly co-ordinated ligands L remain co-ordinated in the products while N–C coupling has occurred. There are many examples of intermolecular attack of nucleophilic nitrogen compounds at CO in metal carbonyls, for example of amines at $[Os_3(CO)_{12}]$.[11–14]

Isomerisation and Protonation Reactions.—To test whether the different structure adopted by compound (**3**) compared with (**1**) is a result of the substitution by PMe_2Ph, we substituted (**1**) by PMe_2Ph. This was best carried out in refluxing heptane (98 °C; u.v. irradiation of a dichloromethane solution of (**1**) and PMe_2Ph at room temperature led to decomposition. The monosubstituted species $[Os_3H(Bu^tCN{=}NNH)(CO)_9(PMe_2Ph)]$ (**4b**) has the structure shown in Scheme 1 (spectroscopic evidence, Table 1). The overall structure of (**1**) is maintained and PMe_2Ph occupies the site shown (J_{PH} = 8.3 Hz). Coupling between the N*H* and hydride nuclei is observed in the ^1H n.m.r. spectrum confirming that the organic ligand has not been modified. Again this is a stable form, not changing in refluxing heptane (6 h) or refluxing nonane (2 h), there being no evidence for cluster (**3**), isomeric with (**4b**), under these conditions.

Since isomers (**3**) and (**4b**) differ in the hydrogen-atom positions, we examined the protonation–deprotonation chemistry of these clusters believing that isomerisation might be induced in this way. Complete protonation of (**3**) in $CDCl_3$ occurs on addition of a five-fold excess of CF_3CO_2H to give the cation (**5a**) in solution which was characterised by its ^1H n.m.r. spectrum (Table 1). The cation like its precursor is a dihydride and the PMe_2Ph co-ordination site has not altered, but the spectrum clearly established that the N–C bond has been ruptured as shown in Scheme 1. Notably the lower-field hydride signal (J_{PH} = 26.4 Hz) shows coupling to the NH proton. Since the nitrogen atom in cluster (**3**) which is protonated has no non-bonding electrons, we propose the reversible N–C bond



Scheme 2. L = CO or PMe_2Ph

cleavage shown in Scheme 2, the species with the opened N–C bond being trapped in acidic solution. The strong i.r. absorption for the $Bu^tCH=NNCO$ ligand at 1 638 cm^{-1} in the solid-state spectrum of compound (3) becomes very weak in solution (1 669 cm^{-1} in cyclohexane and 1 645 cm^{-1} in tetrahydrofuran). This may indicate a solution equilibrium between (3) and the open isomer (Scheme 2) with the latter predominating. Deprotonation of the cation (**5a**) with sodium carbonate regenerates some cluster (3) but also cluster (**4a**), another isomer of (3) and (**4b**), is formed. Cluster (**4a**) has the same nitrogen ligand as (**4b**) but with PMe_2Ph co-ordinated at a site corresponding to that in (3) (see Scheme 1). Compound (**4a**) was difficult to isolate. Chromatography on silica gave (**4a**) as an oily product which readily isomerised to cluster (**4b**). A cyclohexane solution of (**4a**) underwent 40% isomerisation to (**4b**) in 1 d at room temperature and 100% isomerisation after reflux for 1 h.

Protonation of cluster (**4a**) regenerated (**5a**) while protonation of (**4b**) (again using a five-fold excess of CF_3CO_2H in $CDCl_3$ solution) gave cation (**5b**), an isomer of (**5a**). The substitution positions of L (PMe_2Ph) in compounds (3)—(5) were confirmed by the values of J_{PH} for the hydride ligands.

Thus we have been able to convert cluster (3) *via* (**4a**) into (**4b**) and have established that the N–C bond in (3) may be cleaved and reformed.

In three separate identical experiments we showed that cation (**5b**) deprotonates exclusively to cluster (**4b**). However in another experiment, apparently carried out in the same way as the other three, we deprotonated cation (**5b**) to give three neutral products: cluster (**4b**), cluster (3), and a dihydro-cluster which appeared to be just like (3) except with the PMe_2Ph ligand in the site corresponding to that in (**4b**) [hydride signals: δ −15.25 (d, J_{PH} = 9.2 Hz) and −18.08 (d, J_{PH} = 31.1 Hz)]. Clearly three neutral products were obtained in this particular case because conditions for the deprotonation were rather different from those of the other three experiments. Unfortunately we have been unable to define these differences nor repeat this unique experiment.

Experimental

Proton n.m.r. spectra were recorded on a Varian XL200 spectrometer and i.r. spectra on a Perkin-Elmer 983 instrument.

Synthesis of 2,2-*Dimethyldiazopropane*.—This was prepared by the reported method.[7] Trimethylacetaldehyde was treated with toluene-*p*-sulphonylhydrazine to give the hydrazone $Bu^tCH=NNHSO_2C_6H_4Me$-4 as a white crystalline solid (74%) [^1H n.m.r. ($CDCl_3$): δ 1.00 (s), Me_3C; 2.42 (s), 4-Me; 7.04 (s), CH=N; 7.27 (d), and 7.77 (d), C_6H_4]. Treatment of a tetrahydrofuran (thf) solution of the hydrazone with LiBu gave $Li[4-MeC_6H_4SO_2NN{=}CHBu^t]$ as a white solid which was heated under vacuum [*ca.* 1 mmHg (*ca.* 133 Pa)] and a distillate of Bu^tCHN_2 was collected as a yellow-orange liquid. This was stored at −20 °C and used within a few days.

Reaction of Bu^tCHN_2 *with* $[Os_3H_2(CO)_{10}]$.—The diazo-compound (0.936 mmol) was added to a solution of the dihydride (0.100 g, 0.117 mmol) in dichloromethane (10 cm^3) cooled in an ice–water bath. The purple solution became yellow in 15 min and after 1 h the solvent was removed under vacuum and the residue separated by t.l.c. [SiO_2; eluant, light petroleum (b.p. 30—40 °C)] to give one main yellow band which gave $[Os_3H(Bu^tCH=NNH)(CO)_{10}]$ (**1**), as yellow crystals (0.026 g, 23%) from cyclohexane (Found: C, 19.1; H, 1.4; N, 2.9. $C_{15}H_{12}N_2O_{10}Os_3$ requires C, 18.95; H, 1.25; N, 2.95%). A similar reaction carried out in refluxing light petroleum (b.p. 40—60 °C) for 2 h gave a rather better yield (50%). A minor yellow band on the t.l.c. plate gave yellow crystals (0.011 g, 9%) of $[Os_3(CH_2Bu^t)(Bu^tCH=NNH)(CO)_{10}]$ (**2**) (Found: C, 23.95; H, 2.25; N, 2.5. $C_{20}H_{22}N_2O_{10}Os_3$ requires C, 23.55; H, 2.15; N, 2.75%).

Reaction of $[Os_3H(Bu^tCH=NNH)(CO)_{10}]$ (**1**) *with Dimethylphenylphosphine*.—A solution of compound (**1**) (0.100 g, 0.105 mmol) and PMe_2Ph (0.058 g, 0.210 mmol) in n-heptane (15 cm^3) was heated under reflux under nitrogen for 6 h. The i.r. spectrum of the solution indicated that most of (**1**) had reacted. The solvent was removed under reduced pressure and the residue chromatographed [t.l.c.; SiO_2; eluant, light petroleum (b.p. 30—40 °C)–dichloromethane (5:1 v/v)]. The main yellow band was extracted with CH_2Cl_2 and gave yellow crystals (0.0655 g, 59%) of $[Os_3H(Bu^tCH=NNH)(CO)_9(PMe_2Ph)]$ (**4b**), from cyclohexane (Found: C, 25.0; H, 2.25; N, 2.4; P, 3.05. $C_{22}H_{23}N_2O_9Os_3P$ requires C, 24.9; H, 2.2; N, 2.65; P, 2.9%). Heptane or nonane solutions of compound (**4b**) showed no change (i.r. evidence) after heating under reflux for 5 and 2 h respectively.

Preparation of $[Os_3H_2(CO)_9(PMe_2Ph)]$.—A method slightly modified from that reported was used. The addition of PMe_2Ph (0.085 g) to a solution of $[Os_3H_2(CO)_{10}]$ (0.516 g) in light petroleum (b.p. 30—40 °C) (5 cm^3) gave a yellow precipitate of $[Os_3H_2(CO)_{10}(PMe_2Ph)]$ (0.480 g, 86%) on cooling at 0 °C. Hydrogen was bubbled through a suspension of this decacarbonyl (0.470 g) in refluxing n-hexane (100 cm^3) for 1.5 h. Removal of the solvent and t.l.c. [SiO_2; eluant, CH_2Cl_2–light petroleum (b.p. 30—40 °C) (1:3 v/v)] gave a purple-brown band yielding $[Os_3H_2(CO)_9(PMe_2Ph)]$ as purple-brown crystals (0.219 g, 48%), which were characterised by comparison of spectra with those reported.

Reaction of $[Os_3H_2(CO)_9(PMe_2Ph)]$ *with* Bu^tCHN_2.—A solution of Bu^tCHN_2 (0.022 g, 0.224 mmol) and $[Os_3H_2(CO)_9(PMe_2Ph)]$ (0.108 g, 0.112 mmol) in dichloromethane (10 cm^3) was stirred at 0—5 °C. After 30 min it was evaporated to dryness under reduced pressure to give a yellow-brown residue which was chromatographed [t.l.c.; SiO_2; eluant, light petroleum (b.p. 30—40 °C)–diethyl ether (1:1 v/v)]. One main pale yellow band was extracted with dichloromethane which gave $[Os_3H_2(Bu^tCH=NNCO)(CO)_8(PMe_2Ph)]$ (**3**), as pale yellow crystals (0.072 g, 62%) on addition of light petroleum (b.p. 30—40 °C) (Found: C, 24.8; H, 2.2; N, 2.5; P, 2.85. $C_{22}H_{23}N_2O_9Os_3P$ requires C, 24.9; H, 2.2; N, 2.65; P, 2.9%).

Protonation of $[Os_3H_2(Bu^tCH=NNCO)(CO)_8(PMe_2Ph)]$, *Cluster* (**3**).—Trifluoroacetic acid (0.0015 cm^3, 5 mol per mol Os_3) was syringed into a solution of cluster (**3**) (0.004 g) in $CDCl_3$ (0.4 cm^3) at room temperature. The ^1H n.m.r. spectrum was recorded to characterise the cation (**5a**) (Table 1). To neutralise, a solution of sodium carbonate (0.123 g) in water (2 cm^3) was added and the mixture vigorously shaken for 15 min. Chloroform (10 cm^3) was added and the organic layer separated and reduced to dryness under vacuum. The ^1H n.m.r. spectrum of a solution of the solid residue in $CDCl_3$ showed the presence of clusters (**3**) (50%) and (**4a**) (50%). T.l.c. [SiO_2; eluant, light petroleum (b.p. 30—40 °C)–dichloromethane (5:1 v/v)] gave a yellow band yielding compound (**4a**), $[Os_3H(Bu^tCH=NNH)(CO)_9(PMe_2Ph)]$, as a yellow oil which was characterised by the data in Table 1. Treatment of a mixture of clusters (**3**) and (**4a**) (before t.l.c. separation) in $CDCl_3$ with CF_3CO_2H gave a spectrum corresponding to that of cation (**5a**).

Protonation of $[Os_3H(Bu^tCH=NNH)(CO)_9(PMe_2Ph)]$, *Cluster* (**4b**).—Protonation of this compound in the same way as above gave a solution containing only cluster cation (**5b**). Neutralisation with sodium carbonate, also as above, gave only cluster (**4b**) (see Results and Discussion).

Crystal Structure of $[Os_3H_2(Bu^tCH=NNCO)(CO)_8(PMe_2Ph)]$, (**3**).—*Crystal data*. $C_{22}H_{23}N_2O_9Os_3P$, M = 1 061.0, monoclinic, a = 25.480(4), b = 11.747(3), c = 9.978(2) Å, β = 95.72(2)°, U = 2 971.7 Å^3, space group $P2_1/n$, Z = 4, D_c = 2.37 g cm^{-3}, $F(000)$ = 1 935.7, μ(Mo-K_α) = 123.82 cm^{-1}, λ = 0.710 69 Å.

Data collection. Unit-cell parameters and intensity data were obtained at room temperature on a Phillips PW1100 four-circle diffractometer using graphite-monochromated Mo-K_α radiation. The method of data collection and processing was similar to that described earlier.[15] Of the 3 336 unique reflections ($3 \leqslant \theta \leqslant 25°$), 3 034 were considered to be observed [$I_o \geqslant 3\sigma(I_o)$]. A semiempirical absorption correction based on a pseudo-ellipsoid model[16] was applied to the data; 370 azimuthal scan data from 10 independent reflections gave relative transmission factors of 1.000 to 0.535.

Structure solution and refinement.[17] The three Os atoms were located by the heavy-atom method; all remaining non-H atoms were revealed by subsequent refinement and Fourier-difference synthesis. No attempts were made to locate hydrogen atoms, except for the two Os-ring, edge-bridging hydrides. Both hydrogens were visible in a Fourier-difference map, and their positions corroborated by potential-energy-minimisation calculations.[18] For the final full-matrix least-squares refinements, all non-H atoms were assigned anisotropic thermal parameters, the two H atoms were included with isotropic thermal parameters, and weights $w = 1/[\sigma^2(F_o)]$ were applied to the individual reflections. The final values of R and R' were 0.0394 and 0.0372 respectively.

Acknowledgements

We thank the S.E.R.C. for support. Y. F. and K. Hardcastle thank the Department of Industrial Chemistry, Nagasaki University, and the Department of Chemistry, State University of California, Northridge, respectively, for leave.

References

1 R. B. Calvert, J. R. Shapley, A. J. Shultz, J. M. Williams, S. L. Suib, and G. D. Stucky, *J. Am. Chem. Soc.*, 1978, **100**, 6240.
2 R. B. Calvert and J. B. Shapley, *J. Am. Chem. Soc.*, 1978, **100**, 7726.
3 K. Burgess, B. F. G. Johnson, J. Lewis, and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1982, 262.
4 M. R. Churchill and H. J. Wasserman, *Inorg. Chem.*, 1981, **20**, 2905.
5 C. Choo Yin and A. J. Deeming, *J. Chem. Soc., Dalton Trans.*, 1975, 2091.
6 K. A. Azam, A. J. Deeming, I. P. Rothwell, M. B. Hursthouse, and J. D. J. Backer-Dirks, *J. Chem. Soc., Dalton Trans.*, 1981, 2039.
7 G. M. Kaufman, J. A. Smith, G. G. Van der Stouw, and H. Shechter, *J. Am. Chem. Soc.*, 1965, **87**, 935.
8 R. D. Adams and N. M. Golembeski, *J. Organomet. Chem.*, 1979, **171**, C21; R. D. Adams, N. M. Golembeski, and J. P. Selegue, *Inorg. Chem.*, 1981, **20**, 1242.
9 G. Ferguson, W. J. Laws, M. Parvez, and R. J. Puddephatt, *Organometallics*, 1983, **2**, 276.
10 K. Burgess, B. F. G. Johnson, J. Lewis, and P. R. Raithby, *J. Organomet. Chem.*, 1982, **224**, C40; *J. Chem. Soc., Dalton Trans.*, 1982, 2119.
11 C. Choo Yin, K. A. Azam, and A. J. Deeming, *J. Chem. Soc., Dalton Trans.*, 1978, 1201.
12 A. Mayr, Y. C. Lin, N. M. Boag, and H. D. Kaesz, *Inorg. Chem.*, 1982, **21**, 1704.
13 H. D. Kaesz, C. B. Knobler, M. A. Andrews, G. van Buskirk, R. Szostak, C. E. Strouse, Y. C. Lin, and A. Mayr, *Pure Appl. Chem.*, 1984, **54**, 131.
14 A. J. Arce and A. J. Deeming, *J. Chem. Soc., Chem. Commun.*, 1980, 1102.
15 M. K. Cooper, P. A. Duckworth, K. Henrick, and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 1981, 2357.
16 G. M. Sheldrick, EMPABS program, University of Cambridge, 1976.
17 G. M. Sheldrick, SHELX 76 program for crystal structure determination, University of Cambridge, 1976.
18 A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1980, 2509.

Received 9th December 1985; *Paper* 5/2149