Journal of Organometallic Chemistry, 468 (1994) 229–234

Reactivity of triosmium clusters with substituted triphenylphosphines: the crystal and molecular structure of $[HOs_3(CO)_9(2\text{-}PNH)]$ * $(2\text{-}PNH_2 = $ 2-aminophenyldiphenylphosphine)

Eric W. Ainscough, Andrew M. Brodie, Scott L. Ingham and Joyce M. Waters

Department of Chemistry and Biochemistry, Massey University, Palmerston North (New Zealand)

(Received July 7, 1993)

Abstract

The reaction of 2-aminophenyldiphenylphosphine ($2\text{-}PNH_2$) with $[Os_3(CO)_{11}(MeCN)]$ and $[Os_3(CO)_{10}(MeCN)_2]$ has yielded the compounds $[Os_3(CO)_{11}(2\text{-}PNH_2)]$ and $[HOs_3(CO)_9(2\text{-}PNH)]$ respectively. The compounds have been characterized spectroscopically and the structure of one of them $[HOs_3(CO)_9(2\text{-}PNH)]$ determined by an X-ray diffraction study. The ligand bridges an edge of the triosmium triangle with the P atom bound to a single Os atom in an equatorial site. The amido N forms a bridge between this Os atom and one of its neighbours in the triangle.

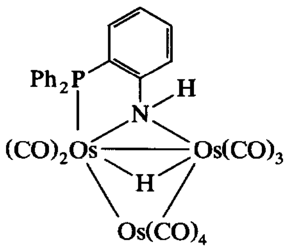
Key words: Triosmium; Cluster; Phosphine

1. Introduction

The chemistry of phosphine-containing ligands with mixed functionality has received much less attention than that of their unsubstituted phosphine counterparts. Some studies of complexes of transition metals with ligands such as 2-hydroxophenyldiphenylphosphine [1] and 2-aminophenyldiphenylphosphine [2–4] have been reported, but few, if any, studies have been made with transition metal clusters. We report here our findings on the reaction between the ligand 2-aminophenyldiphenylphosphine ($2\text{-}PNH_2$) and the substituted triosmium clusters $[Os_3(CO)_{11}(MeCN)]$ and $[Os_3(CO)_{10}(MeCN)_2]$.

2. Results and discussion

The activated cluster $[Os_3(CO)_{11}(CH_3CN)]$ reacts readily with one equivalent of the substituted triphenylphosphine ligand, $2\text{-}PNH_2$, to yield the monophosphine cluster $[Os_3(CO)_{11}(2\text{-}PNH_2)]$. This compound is stable in air and in solution and has been characterized spectroscopically. The IR spectrum is very similar to those of other tertiary phosphine clusters of the type $[Os_3(CO)_{11}(PR_3)]$ [5], and thus we can conclude that the ligand coordinates via the phosphorus atom only, acting as a two-2 electron donor and occupying an equatorial site in the triosmium frame. In contrast, the disubstituted cluster $[Os_3(CO)_{10}(CH_3CN)_2]$, on reaction with the same difunctional ligand in equimolar amounts, yields a complex mixture of products. Two of the major species produced have been fully characterized. The first of these, $[HOs_3(CO)_9(2\text{-}PNH)]$, has the ligand bridging an edge of the triosmium triangle with the amido N shared between the two Os atoms of the edge and the phosphorus atom coordinated to one of these metals.



This arrangement has been demonstrated by single-crystal X-ray diffraction. Deprotonation of the aniline

---

Correspondence to: Professor A.M. Brodie.

* 1,1,2,2,2,3,3,3,3-Nonacarbonyl-1,2-μ-2-benzamidodiphenylphosphine-1,2-μ-hydrido-*triangulo*-triosmium.

0022-328X/94/\$7.00
SSDI 0022-328X(93)24050-F

moiety occurs by hydride transfer to the triosmium triangle, the resulting metal hydride probably bridging the same edge of the cluster as does the amido phosphine ligand. The 2-PNH$^-$ ligand is therefore behaving as a five-electron donor, but it is unusual in that it bridges only one edge of the cluster rather than bonding to all three osmium atoms [6]. A second product is the compound [$Os_3(CO)_{11}$(2-PNH_2)], identical with that isolated from the reaction of 2-PNH_2 with [$Os_3(CO)_{11}$(MeCN)]. Further work is underway to characterize other products in the mixture.

2.1. Single-crystal X-ray structural analysis of [$HOs_3(CO)_9$(2-PNH)]

A thermal ellipsoid diagram of [$HOs_3(CO)_9$(2-PNH)], including the numbering system, is shown in Fig. 1. Fractional coordinates are listed in Table 1 and selected bond distances and angles in Table 2. The three osmium atoms define a triangle with the P atom terminally coordinated to one of the metal atoms and the amido N bridging between this osmium atom and one of its metal neighbours. The Os–Os distances of 2.801(1), 2.846(1) and 2.850(1) Å are all slightly shorter than the average metal–metal distance of 2.877(3) Å found in $Os_3(CO)_{12}$ [6], but they are similar to metal–metal distances reported for other 48-electron clusters [7,8]. The shortest of the three (Os(1)–Os(2)) is probably a result of the steric requirements of the ligand bridging an edge of the triosmium triangle. The phosphorus atom coordinates to Os(1) at a distance of 2.319(2) Å, which lies within the range of osmium–phosphorus bond lengths observed for other terminally coordinated tertiary phosphines [9]. The Os(1)–Os(2) edge of the cluster is bridged by the N atom of the coordinated amido group, with osmium–nitrogen distances to Os(1) and Os(2) of 2.137(6) and 2.161(6) Å respectively. These bond lengths are similar to those observed in [$H_2Os_3(CO)_9(NHC_6H_3F)$] [10], in which a benzamido N bridges one edge of the cluster with Os–N distances of 2.112(10) and 2.143(11) Å. The phosphorus atom lies out of the triosmium plane by only 0.21 Å and thus may be considered to occupy an equatorial site on the cluster. This is in agreement with the general observation that tertiary phosphines only occupy such sites on the triosmium frame [6]. In contrast, the amido N is out of the plane defined by the osmium triangle by 1.54 Å. The plane containing the atoms Os(1), Os(2), N makes an angle of 71° with the plane in which the three metal atoms lie. The atoms P,N,C(011) and C(012) are approximately coplanar,

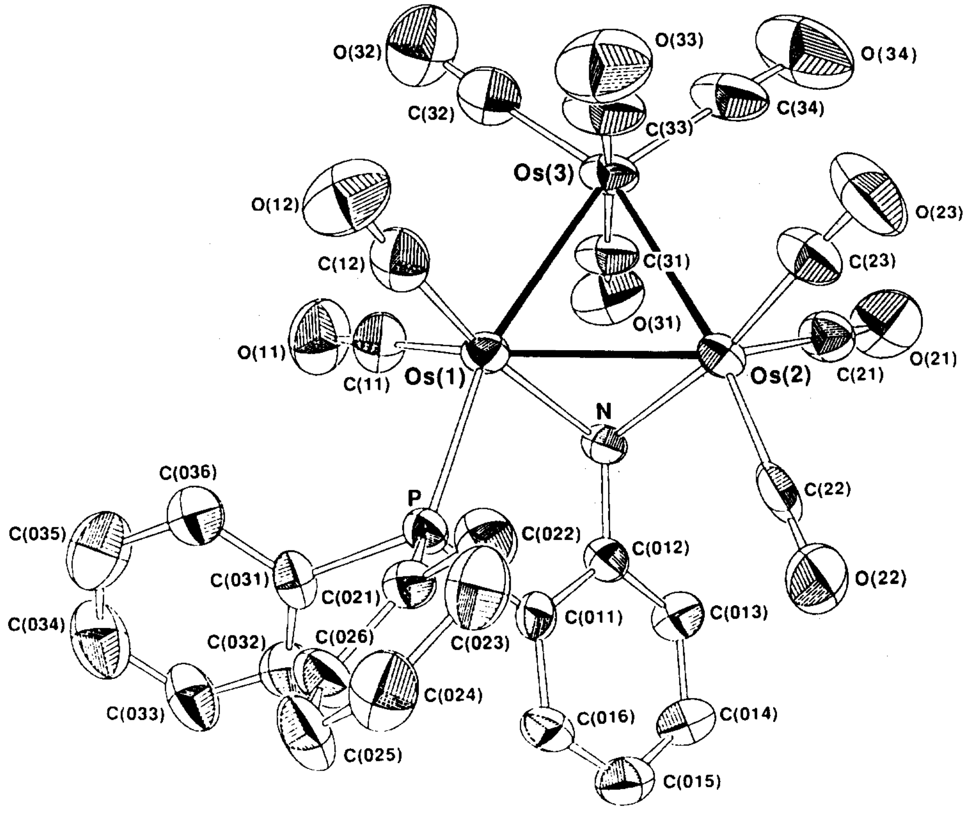


Fig. 1. Structure of [$HOs_3(CO)_9$(2-PNH)], showing the numbering system. Ellipsoids are drawn at the 50% probability level.

TABLE 1. Fractional atomic coordinates for [$HOs_3(CO)_9$(2-PNH)] with estimated standard deviations in parentheses

Os(1)	0.28373(3)	0.19836(2)	0.35242(2)
Os(2)	0.32701(3)	0.07452(2)	0.26882(2)
Os(3)	0.48539(3)	0.18965(2)	0.30188(3)
P	0.1014(2)	0.1807(1)	0.3625(2)
N	0.1865(5)	0.1517(3)	0.1983(5)
O(11)	0.2316(8)	0.3496(4)	0.2934(7)
O(12)	0.4474(7)	0.2314(5)	0.5851(6)
O(21)	0.3624(7)	0.0386(4)	0.0701(6)
O(22)	0.1457(7)	−0.0378(3)	0.2593(7)
O(23)	0.5415(7)	−0.0175(5)	0.4026(7)
O(31)	0.3125(7)	0.2403(4)	0.0788(6)
O(32)	0.5857(9)	0.3350(4)	0.3738(8)
O(33)	0.6211(7)	0.1302(5)	0.5304(6)
O(34)	0.6543(8)	0.1209(7)	0.2249(8)
C(11)	0.2522(9)	0.2915(5)	0.3176(8)
C(12)	0.3840(9)	0.2201(5)	0.4963(8)
C(21)	0.3480(8)	0.0514(5)	0.1448(7)
C(22)	0.2130(8)	0.0045(5)	0.2630(8)
C(23)	0.4619(8)	0.0178(5)	0.3529(8)
C(31)	0.3749(8)	0.2216(5)	0.1623(8)
C(32)	0.5448(9)	0.2806(6)	0.3464(9)
C(33)	0.5694(8)	0.1530(7)	0.4457(8)
C(34)	0.5907(9)	0.1494(7)	0.2522(9)
C(011)	0.0149(7)	0.1314(4)	0.2411(6)
C(012)	0.0648(7)	0.1270(4)	0.1687(6)
C(013)	−0.0017(7)	0.0969(4)	0.0673(6)
C(014)	−0.1117(8)	0.0689(4)	0.0434(7)
C(015)	−0.1598(8)	0.0700(5)	0.1162(7)
C(016)	−0.0959(7)	0.1013(4)	0.2160(6)
C(021)	0.0920(6)	0.1311(4)	0.4714(6)
C(022)	0.1700(8)	0.0775(4)	0.5197(7)
C(023)	0.1599(9)	0.0394(4)	0.5986(8)
C(024)	0.0681(9)	0.0532(5)	0.6313(8)
C(025)	−0.0109(9)	0.1054(5)	0.5844(8)
C(026)	−0.0005(8)	0.1450(5)	0.5027(7)
C(031)	0.0104(8)	0.2570(4)	0.3569(6)
C(032)	−0.1082(8)	0.2671(4)	0.2830(8)
C(033)	−0.1696(9)	0.3244(6)	0.2866(8)
C(034)	−0.1160(10)	0.3750(6)	0.3614(9)
C(035)	0.0001(11)	0.3660(5)	0.4369(9)
C(036)	0.0654(9)	0.3097(4)	0.4344(8)

TABLE 2. Selected bond lengths (Å) and bond angles (°) for [$HOs_3(CO)_9$(2-PNH)] with estimated standard deviations in parentheses

Bond lengths			
Os(1)–Os(2)	2.801(1)	Os(1)–N	2.137(6)
Os(1)–Os(3)	2.846(1)	Os(2)–N	2.161(6)
Os(2)–Os(3)	2.850(1)	N–C(012)	1.443(9)
Os(1)–P	2.319(2)	N–H(N)	1.188(6)
Bond angles			
Os(1)–Os(2)–Os(3)	60.5(1)	Os(1)–P–C(011)	102.2(2)
Os(1)–Os(3)–Os(2)	58.9(1)	Os(1)–P–C(021)	122.1(2)
Os(2)–Os(1)–Os(3)	60.6(1)	Os(1)–P–C(031)	117.7(3)
Os(2)–Os(1)–P	105.0(1)	Os(1)–N–Os(2)	81.4(2)
Os(3)–Os(1)–P	164.8(1)	Os(1)–N–H(N)	95.5(3)
Os(2)–Os(1)–N	49.7(2)	Os(2)–N–H(N)	122.0(4)
Os(3)–Os(1)–N	84.1(2)	Os(1)–N–C(012)	118.8(5)
Os(1)–Os(2)–N	48.9(2)	Os(2)–N–C(012)	115.0(4)
Os(3)–Os(2)–N	84.1(2)	C(012)–N–H(N)	116.7(5)
N–Os(1)–P	83.6(2)		

with Os(1) lying 0.18 Å out of this plane. The N–C(012) bond length is 1.443(9) Å which is in accord with the corresponding distance (1.459(14) Å) reported for the cluster [$H_2Os_3(CO)_9(NHC_6H_3F)$] [10]. The range of Os–C and C–O bond lengths and angles observed lie within the limits expected from data observed in other osmium carbonyl clusters [11,12].

There have been several reported structural determinations that involve either the neutral phosphine, 2-PNH_2 [3,13], or its deprotonated form, 2-PNH^- [3,14–16]. In these complexes, in all but one case, the ligands coordinate in a bidentate manner through the phosphorus and nitrogen atoms. In the dinuclear rhodium(II) complex [{Rh(μ-2-PNH)(CO)Cl}$_2$] · EtOH the 2-PNH^- ligands bridge the rhodium–rhodium bond in a manner similar to that found in [$HOs_3(CO)_9$(2-PNH)], with the two amido nitrogen atoms bridging the metal atoms and the phosphorus atoms each coordinat-

TABLE 3. ^1H NMR data (δ (ppm)) [a]

	Aryl-H	N-H	Os-H
2-PNH_2	7.28–7.36 (m, 10H) 7.17 (ddd, $J = 7.9, 7.0, 1.7$, 1H) 6.65–6.78 (m, 3H)	4.14 (s, broad, 2H)	–
[$Os_3(CO)_{11}$(2-PNH_2)]	7.53–7.62 (m, 4H) 7.40–7.46 (m, 6H) 7.25–7.31 (m, 1H) 6.93–7.01 (m, 1H) 6.72–6.84 (m, 2H)	3.85 (s, broad, 2H)	–
[$HOs_3(CO)_9$(2-PNH)]	7.64–7.72 (m, 2H) 7.24–7.53 (m, 11H) 7.06 (t, $J = 7.3$, 1H)	5.90 (s, broad, 1H)	−14.65 (dd, $J = 8.4, 2.7$, 1H)

[a] In $CDCl_3$ at 25°C, J in Hz.

TABLE 4. ^{13}C NMR data for aryl rings (δ (ppm)) [a]

No.	2-PNH_2	$[Os_3(CO)_{11}(2\text{-}PNH_2)]$	$[HOs_3(CO)_9(2\text{-}PNH)]$
1	135.4 (7.8)	133.7 (46.9)	134.2 (58.6); 131.6 (50.8) [b]
2	133.7 (18.8)	133.2 (11.8)	133.1 (19.6); 131.3 (11.7) [b]
3	128.6 (7.7)	128.7 (11.7)	129.1 (9.8); 129.1 (9.7) [b]
4	128.8	130.9	132.8
5	119,4 (8.6)	115.8 (54.7)	123.2 (50.8)
6	149.8 (19.7)	147.4 (5.9)	[c]
7	115.4 (2.6)	117.3 (5.8)	124.2 (9.7)
8	130.4	132.4	131.2
9	118.7 (1.7)	118.6 (9.8)	125.4 (5.9)
10	134.3 (2.6)	133.1 (11.7)	130.6 (2.3)

[a] In $CDCl_3$ at 25°C; J(P–C) (Hz) in parentheses; see Fig. 2 for assignments.

[b] These resonances are no longer equivalent.

[c] This resonance appears amongst the carbonyl resonances and could not be unambiguously assigned (see text).

ing to one Rh atom [16]. As for the osmium complex, the geometry around the amido nitrogen is approximately tetrahedral.

2.2. *NMR spectrum of* $[Os_3(CO)_{11}(2\text{-}PNH_2)]$

The ^{1}H NMR resonances observed for the cluster $[Os_3(CO)_{11}(2\text{-}PNH_2)]$ show only minor changes in chemical shift parameters associated with the arene protons relative to the uncoordinated ligand. These data are summarized in Table 3. A broad resonance attributable to the amino protons was observed at *ca.* 3.85 ppm. The ^{13}C data for the arene carbon atoms of the complex and the free ligand are given in Table 4, and Fig. 2 shows the numbering scheme used. In general, the changes in chemical shifts for these carbon atoms on coordination are also relatively small. The largest decrease in frequency is observed for the *ipso* carbon atoms C_1 and C_5 and for the *ortho* carbon C_6. The first two of these resonances also show a dramatic increase in the ^{31}P–^{13}C coupling on coordination (to *ca.* 50 Hz from *ca.* 8 Hz for the free ligand). Shifts of about 2 ppm to higher frequency are observed for the carbon atoms C_4 and C_8, which are *para* to the *ipso* carbon atoms, and for C_7. At room temperature two broad resonances (*ca.* 171 and 183 ppm), attributable to the carbonyl ligands, were noted. This lack of sharp peaks is due to the rapid intramolecular scrambling of the equatorial and axial carbonyl ligands [17]. On cooling these samples to −50°C, eight resonances were observed with an intensity ratio of 2 : 2 : 2 : 1 : 1 : 1 : 1 : 1. The chemical shifts are similar to those found for $[Os_3(CO)_{11}(PEt_3)]$ [17] and have been assigned (Fig. 2) accordingly (δ = 192.1 (A), 183.2 (B), 185.7 (C), 175.5 (D), 172.0 (E), 171.3 (F), 169.2 (G) and 176.1 (H) ppm). Only the resonance assigned A shows splitting due to ^{31}P–^{13}C coupling (7.8 Hz).

2.3. *NMR spectrum of* $[HOs_3(CO)_9(2\text{-}PNH)]$

The ^{1}H NMR spectrum of $[HOs_3(CO)_9(2\text{-}PNH)]$ (Table 3) shows the osmium-hydride resonance as a doublet of doublets at −14.65 ppm, a value which is consistent with a bridging hydride. The ^{31}P coupling (J = 8.4 Hz) indicates that the hydride must bridge an edge of the triosmium triangle to which a phosphorus nucleus is attached, and the coupling to the amido NH proton (J = 2.7 Hz) suggests that it bridges the same edge as the amido nitrogen. The hydride resonance is similar to that observed for the benzamido complex $[HOs_3(CO)_{10}(C_6H_5NH)]$ (δ = −14.13 ppm, J = 3.1 Hz) [18]. A broad resonance at 5.90 ppm is attributed to the amido proton, and resonances attributed to the aromatic protons of the ligand were identified in the range 7.06–7.72 ppm. The single peak at 25.8 ppm in

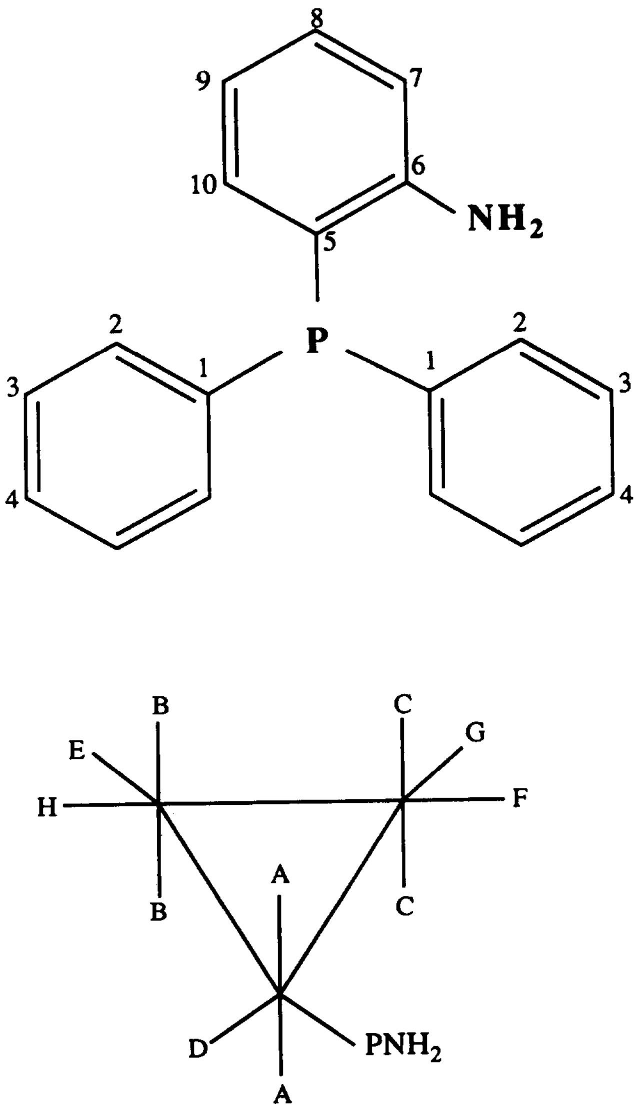


Fig. 2. Labelling schemes used for the ^{13}C NMR assignments.

the ^{31}P NMR spectrum is consistent with a coordinated phosphine.

The ^{13}C NMR spectrum (Table 4) exhibits a complicated multiplet of signals in the aromatic region from 120 to 140 ppm. The two unsubstituted phenyl rings are not equivalent, in contrast with the case for $[Os_3(CO)_{11}(2\text{-}PNH_2)]$, and hence separate resonances are observed for each ring. This lack of equivalence is due to the coordination of the amino substituent of the ligand. No resonance attributable to C_6 (the atom to which the N substituent is attached) was observed in the aromatic region. However eleven resonances were seen in the range 170–200 ppm (δ = 191.4, 187.2, 182.1, 177.7, 177.5, 177.2, 177.0, 174.1, 173.5, 173.1 and 170.3 ppm), which is two more than expected for the nine carbonyl ligands. It is likely that the two additional signals are attributable to the doublet expected for C_6, but this resonance was not unambiguously assigned. One resonance (δ = 187.2 ppm) exhibits a small coupling of 4.0 Hz, and was thus assigned to a carbonyl group adjacent to the P.

3. Experimental details

The mono- and di-substituted precursor clusters, $[Os_3(CO)_{11}(CH_3CN)]$ and $[Os_3(CO)_{10}(CH_3CN)_2]$, were prepared by the reaction of $[Os_3(CO)_{12}]$ with trimethylamine-*N*-oxide in acetonitrile as described previously [19]. The ligand, 2-PNH_2, was also prepared by a published method [20].

NMR measurements were performed on a JEOL GX270W spectrometer. IR spectra were recorded on a BIO-RAD FTS-40 instrument from samples in cyclohexane solutions using 0.5 ml NaCl solution cells. Mass spectra were obtained using a Varian VG70-250S double focusing magnetic sector spectrometer by the liquid secondary ion mass spectrometry (LSIMS) method. The samples were dissolved in CH_2Cl_2 with *m*-nitrobenzylalcohol used as a matrix. Isotope abundance calculations were performed to identify the parent ion. Microanalyses were performed by the Campbell Microanalytical Laboratory, University of Otago.

3.1. Reaction of $[Os_3(CO)_{11}(CH_3CN)]$ with 2-PNH_2

To a dichloromethane solution (20 ml) of $[Os_3(CO)_{11}(CH_3CN)]$ (46 mg, 0.05 mmol) was added a solution of 14 mg (0.05 mmol) of 2-PNH_2 in 15 ml of CH_2Cl_2. The mixture was refluxed for 5 min and then allowed to cool to room temperature. The solvent was removed under vacuum and the residue purified by thin layer chromatography (TLC) (yield, 51 mg, 88%). Yellow–orange crystals of $[Os_3(CO)_{11}(2\text{-}PNH_2)]$ were obtained by recrystallization from CH_2Cl_2–*n*-hexane. Anal. Found: C, 30.62; H, 1.52; N, 1.01; P, 2.94; $C_{29}H_{16}NO_{11}Os_3P$ calc.: C, 30.13; H, 1.40; N, 1.21; P, 2.68%. IR: $\nu(CO)$ 2107m, 2054s, 2036ms, 2019vs, 2001m, 1990m, 1979m, 1960w cm^{-1}. MS: m/z 1161 ($M^+(^{192}Os)$).

3.2. Reaction of $[Os_3(CO)_{10}(CH_3CN)_2]$ with 2-PNH_2

To a dichloromethane solution (20 ml) of $[Os_3(CO)_{10}(CH_3CN)_2]$ (52 mg, 0.056 mmol) was added a solution of 2-PNH_2 (15 mg, 0.054 mmol) in 10 ml of CH_2Cl_2. The mixture was refluxed for 5 min and then allowed to cool to room temperature. The solvent was removed under vacuum and the residue was purified by TLC with a mixture of 75% CH_2Cl_2 and hexane as eluent to yield four major products. The first two bands after further purification by TLC (eluting with a 35% CH_2Cl_2–*n*-hexane mixture) gave $[HOs_3(CO)_9(2\text{-}PNH)]$ (yield, 11%) and $[Os_3(CO)_{11}(2\text{-}PNH_2)]$ (yield, 12%). Yellow and yellow–orange crystals of these clusters respectively were obtained by recrystallization from CH_2Cl_2–*n*-hexane. The latter cluster is identical to that obtained from the reaction between $[Os_3(CO)_{11}(CH_3CN)]$ and 2-PNH_2 described above. Chemical analysis and spectroscopic results for $[HOs_3(CO)_9(2\text{-}PNH)]$ are given. Anal. Found: C, 30.11; H, 1.51; N, 1.27; $C_{27}H_{16}NO_9Os_3P$ calc.: C, 29.48; H, 1.47; N, 1.27%. IR: $\nu(CO)$ 2087s, 2049vs, 2008s, 1994s, 1985m, 1974m, 1969s cm^{-1}. MS: m/z 1105 ($M^+(^{192}Os)$).

3.3. Single-crystal X-ray structural determination of $[HOs_3(CO)_9(2\text{-}PNH)]$

Crystal data and data pertaining to data collection and structure refinement are given in Table 5 for $[HOs_3(CO)_9(2\text{-}PNH)]$. A crystal suitable for diffraction studies was grown from an *n*-hexane–CH_2Cl_2 mixture and mounted on a glass fibre on an Enraf-Nonius CAD4 diffractometer equipped with graphite-monochromated Mo Kα radiation. Intensity data were collected at 293° in the ω–2θ mode to $\theta_{max} = 25°$ ($+h$, $+k$, $\pm l$) and corrected for Lorentz and polarization effects. Crystal stability was monitored hourly by the observation of the intensities of three standard reflections. Crystal decay was linear (2.6%) and the data were corrected accordingly. Empirical absorption corrections were based on Ψ scans with minimum and maximum corrections of 0.819 and 1.000 being calculated. Structure solutions were obtained by Patterson and Fourier methods and refinement of the structures was by the full-matrix least-squares method [21]. Atomic scattering factors for Os were from the listings of Cromer and Mann [22]; anomalous dispersion terms were from Cromer and Liberman [23]. All non-hydrogen atoms were refined assuming anisotropic thermal motion. Phenyl ring hydrogen atoms were placed in

TABLE 5. Crystallographic data for [$HOs_3(CO)_9$(2-PNH)]

Formula	$C_{27}H_{16}NO_9Os_3P$
M	1100.00
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	12.236(3)
b (Å)	19.280(7)
c (Å)	13.824(2)
β (°)	115.69(1)
U (Å^3)	2938.6
Z	4
D_c (g cm^{-3})	2.486
μ(Mo Kα) (cm^{-1})	130.6
F(000)	2000
θ_{max} (°)	25
Unique data	4855
Indices explored	$+h$, $+k$, $\pm l$
Merging R (based on I)	0.024
Data with $F_o^2 \geq 3\sigma(F_o)^2$	3782
Parameters refined	373
R [a]	0.028
R_w [a]	0.031
Weighting scheme: k, g [a]	1.000, 0.00148
Largest shift (e.s.d.)	0.06
Highest peak in difference map (e Å^3)	1.04

[a] $R = \Sigma|(|F_o| - |F_c|)|/\Sigma|F|$;
$R = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = k/[\sigma^2(|F_o|) + g \cdot |F_o|^2]$.

calculated sites (C–H, 0.96 Å) and were constrained to ride on their associated carbon atoms with overall isotropic thermal parameters refined for each ring. The thermal parameters of these H atoms were fixed. The bridging hydrogen in the cluster was not located, but the amido hydrogen (H(N)) was clearly visible on a difference electron density map at a distance of 1.19 Å from the nitrogen atom. Its position was not refined.

Tables of hydrogen atom coordinates, thermal parameters and a complete list of bond lengths and angles, have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgments

We thank Massey University for the award of a Ph.D. Postgraduate Scholarship (to S.L.I.), Mr. P. Loveday, University of Cambridge for the preparation of osmium carbonyl, Mr. J. Allen, Horticulture and Food Research Institute of NZ Ltd. for mass spectra, and the New Zealand Lottery Grants Board for financial assistance.

References

1 T.B. Rauchfuss, *Inorg. Chem.*, *16* (1977) 2966.
2 M.K. Cooper, P.A. Duckworth, T.W. Hambley, G.J. Organ, K. Hendrick, M. McPartlin and A. Parekh, *J. Chem. Soc., Dalton Trans.*, (1989) 1067.
3 G.J. Organ, M.K. Cooper, K. Henrick and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, (1984) 2377.
4 M.K. Cooper and J.M. Downes, *Inorg. Chem.*, *17* (1978) 880.
5 A.J. Deeming, B.F.G. Johnson and J. Lewis, *J. Chem. Soc. (A)*, (1970) 897.
6 A.J. Deeming, *Adv. Organomet. Chem.*, *26* (1986) 1.
7 K. Burgess, B.F.G. Johnson, J. Lewis and P.R. Raithby, *J. Chem. Soc., Dalton Trans.*, (1982) 2025.
8 M.J. Mays, F. Pavelčík, P.R. Raithby, P.L. Taylor and P.J. Wheatley, *Acta Crystallogr., Sect. B, 37* (1981) 2228.
9 M.I. Bruce, M.J. Liddell, C.A. Hughes, B.W. Skelton and A.H. White, *J. Organomet. Chem.*, *347* (1988) 157.
10 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.
11 P.A. Jackson, B.F.G. Johnson, J. Lewis, A.D. Massey, D. Braga, C. Gradella and F. Grepioni, *J. Organomet. Chem.*, *391* (1990) 225.
12 M.R. Churchill and R.A. Lashewycz, *Inorg. Chem.*, *18* (1979) 848.
13 M.K. Cooper, J.M. Downes, H.J. Goodwin and M. McPartlin, *Inorg. Chim. Acta*, *76* (1983) L157.
14 C.N.G. Ansell, M. McPartlin, P.A. Tasker, M.K. Cooper and P.A. Duckworth, *Inorg. Chim. Acta*, *76* (1983) L135.
15 M.K. Cooper, J.M. Downes, H.J. Goodwin, M. McPartlin and J.M. Rosalky, *Inorg. Chim. Acta*, *76* (1983) L155.
16 M.K. Cooper, G.J. Organ, P.A. Duckworth, K. Henrick and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, (1988) 2287.
17 B.F.G. Johnson, J. Lewis, B.E. Reichert and K.T. Schorpp, *J. Chem. Soc., Dalton Trans.*, (1976) 1403.
18 C.C. Yin and A.J. Deeming, *J. Chem. Soc., Dalton Trans.*, (1974) 1013.
19 S.R. Drake and R. Khattar, *Organomet. Synth.*, *4* (1988) 234.
20 M.K. Cooper, J.M. Downes and P.A. Duckworth, *Inorg. Synth.*, *25* (1989) 129.
21 G.M. Sheldrick, SHELX-76 *Program for Crystal Structure Determination*, University of Cambridge, UK, 1976.
22 D.T. Cromer and J.B. Mann, *Acta Crystallogr., Sect. A, 24* (1968) 321.
23 D.T. Cromer and D. Liberman, *J. Chem. Phys.*, *53* (1970) 1891.