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DINUCLEAR AND TRINUCLEAR COMPOUNDS OF OSMIUM WITH FORMAMIDINATO LIGANDS

ANTONY J. DEEMING * and ROY PETERS

Department of Chemistry, University College London, 20 Gordon Street, London WC1H OAJ (Great Britain)

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Summary

Reactions of $[Os_3(CO)_{12}]$ or $[Os_3(CO)_{10}L_2]$ (L = cyclooctene) with the formamidines RNHCH=NR (R = isopropyl or benzyl) have given various formamidinato complexes. The complex $[Os_3H(CO)_{10}(\mu_2\text{-}PhCH_2NCHNCH_2Ph)]$ thermally and reversibly decarbonylates with *ortho*-metallation at one benzyl group. The complex $[Os_3H(CO)_9(\mu_3\text{-}PhCH_2NCHNCH_2Ph)]$ was not characterised whereas the isopropyl analogue was easily obtained and shown to be stereochemically rigid with non-equivalent NPr^i groups. Dimethylphenylphosphine addition and protonation reactions are described. Under the most vigorous conditions the dinuclear compounds $[Os_2(CO)_6(\mu_2\text{-}RNCHNR)_2]$ (R = Pr^i or $PhCH_2$) are formed.

Introduction

N,N-Dialkylformamidines RNHCH=NR may be regarded formally as nitrogen analogues of formic acid and we have prepared a series of di- and tri-nuclear osmium compounds, **1** to **8**, containing *N,N*-dialkylformamidinato ligands derived from RNHCH=NR (R = Pr^i or $PhCH_2$). Some of these are analogues of known carboxylato complexes. Thus neat boiling acetic acid reacts rapidly and quantitatively with $[Os_3(CO)_{12}]$ to give $[Os_2(CO)_6(MeCO_2)_2]$ [1] while using milder conditions trinuclear compounds are accessible as in the formation of $[Os_3H(CO)_{10}(MeCO_2)]$ by reacting acetic acid with $[Os_3(CO)_{10}L_2]$ (L = MeCN or L_2 = cyclohexa-1,3-diene) [2]. We will now describe formamidinato analogues of both of these acetato compounds. In the trinuclear as well as the dinuclear acetato compounds, the acetato ligand is doubly bridging but with the nitrogen analogues triply bridging is found as well. The mixed O,N-ligands are also known as in $[Os_3H(CO)_{10}(RNCHO)]$ [3—5] and recently decarbonylation of the compound with R = H in refluxing nonane has been shown to give

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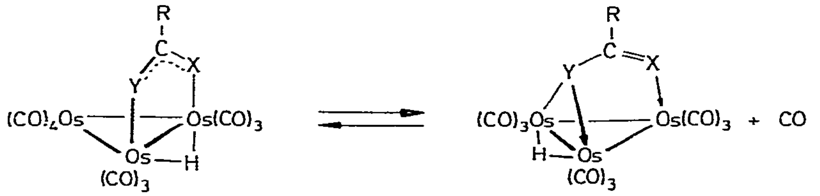


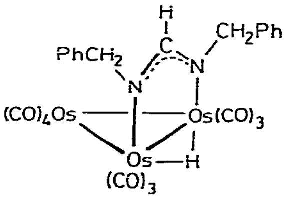
(1)

X = Y = O
X = Y = NR′
X = O ; Y = NR′

the cluster $[Os_3H(CO)_9(\mu_3\text{-}NHCHO)]$ [5]. Equation 1 shows a generalised interconversion of μ_2- and μ_3- forms of the ligands. The tendency of complexes of type $[Os_3H(CO)_{10}(RCXY)]$ to decarbonylate to give $[Os_3H(CO)_9(RCXY)]$ is greater when X = Y = NR than when Y = NR and X = O. When X = Y = O there is no evidence for the nonacarbonyl being formed.

Results

Oxidative addition of $PhCH_2NHCH{=}NCH_2Ph$ at $[Os_3(CO)_{10}L_2]$ (L = cyclooctene) gave a fairly low yield (15%) of the compound $[Os_3H(CO)_{10}(PhCH_2NCHNCH_2Ph)]$ (**1**), and no other compound in significant quantities. The structure shown is like that of $[Os_3H(CO)_{10}(RCO_2)]$ and is based on spectroscopic evidence. The two $PhCH_2$ groups are equivalent but the CH_2 protons are diastereotopic. This means that the two nitrogen atoms are fixed since, if they rapidly interchanged their positions, the CH_2 atoms would exchange since there would be a time-averaged plane of symmetry through the ligands.



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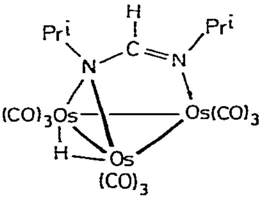

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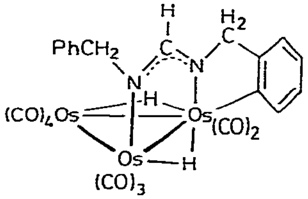

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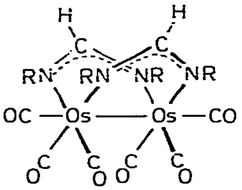
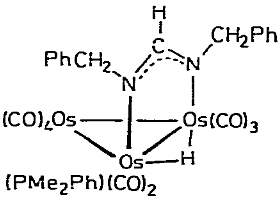


(4) (R = PhCH$_2$)

(5) (R = Pr^i)



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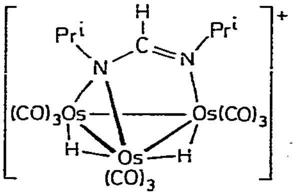
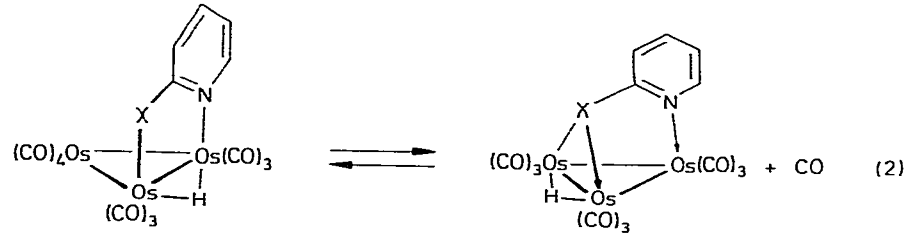


(8)

We expected complex **1** to decarbonylate thermally in the same way that $[Os_3H(CO)_{10}(\mu_2\text{-}NHCHO)]$ gave $[Os_3H(CO)_9(\mu_3\text{-}NHCHO)]$ (eq. 1; X = O; Y = NH) [5]. A similar decarbonylation of $[Os_3H(CO)_{10}(\mu_2\text{-}ArNCHS)]$ gives $[Os_3H(CO)_9(\mu_3\text{-}ArNCHS)]$, except that in this case the ligand in the decacarbonyl is bridging two osmium atoms just through the sulphur atom [10]. Another reaction of this type is shown in eq. 2 where compounds **10** formed by oxidative addition of pyridone or 2-aminopyridine at triosmium clusters decarbonylate thermally and reversibly to give the nonacarbonyl compounds **11**. An X-ray structure of **11** (X = NH) has been determined [11]. Although **1** decarbonylates thermally in refluxing octane it does so with *ortho*-metallation of one of the benzyl groups with the formamidinato-bridge remaining essentially undisturbed. Compound **3** formed in this way is believed to have the structure shown. The benzyl groups are no longer equivalent and the two CH_2 groups give two separate AB quartets in the ^1H NMR spectrum. The compound is a dihydride and although the phenyl resonances were not analysed the complexity is consistent with *ortho*-metallation. Treatment of **3** with CO reverses the decarbonylation *.



(10) (X = O or NH) (11)

Compound **3** is not of a totally new type since the *ortho*-metallated compounds **12** and **13** are known [9,12]. The difference is that compounds **12** and **13** have a single atom bridge between osmium atoms. We were unable to thermally decarbonylate **3** any further to *ortho*-metallate the remaining benzyl group.

Compound **3** was also obtained by reacting $PhCH_2NHCH{=}NCH_2Ph$ directly with $[Os_3(CO)_{12}]$ in refluxing octane but then an equal amount (37%) of a

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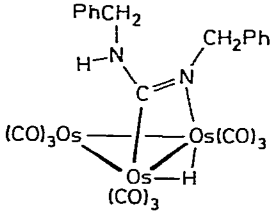

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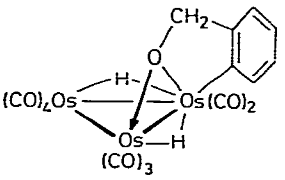

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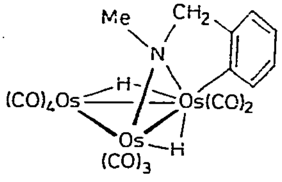

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[*] The reaction of **3** with CO at 125°C generates compound **1** mainly but a very minor yellow chromatographic band has an infrared spectrum (2085m, 2054s, 2028s, 2000s, 1980s, 1966m, 1951m cm^{-1} in cyclohexane) very like that of **2** (Table 1). This compound is probably $[Os_3H(CO)_9(\mu_3\text{-}PhCH_2NCHNCH_2Ph)]$ but too little material was available to confirm this.

TABLE 1

INFRARED AND ^{1}H NMR DATA

Compound	ν(CO) (cm^{-1}) ^{a}			^{1}H NMR ^{b} δ (ppm)	Assign	J (Hz)
$[Os_3H(CO)_{10}(PhCH_2NCHNCH_2Ph)]$	2106m,	2065s,	2055s,	7.87d	NC*H*N	2
(1)	2022s,	2004s,	1995m,	7.14m	Ph	
	1986mw,	1975mw		7.29m	Ph	
				3.66d	CH_2	14
				3.26d	CH_2	14
				−12.91d	Os*H*	2
$[Os_3H(CO)_9(\mathrm{Pr}^iNCHN\mathrm{Pr}^i)]$	2084m,	2064s,	2027s,	9.03s	NC*H*N	
(2)	1999s,	1989vw,	1980s,	3.48m	$CHMe_2$	7
	1965m,	1950m,	1937vw	2.37m	$CHMe_2$	7
				1.10d	CH_3	7
				1.03d	CH_3	7
				−11.46s	Os*H*	
$[Os_3H_2(CO)_9(C_6H_4CH_2NCHNCH_2Ph)]$ ^{c}	2092m,	2058s,	2028s,	9.48s	NC*H*N	
(3)	2010s,	2004m,	1985m,	7.0m, 7.2m	C_6H_4,	
	1964m			7.4 m, 7.8m	C_6H_5	
				4.79d 4.33d	CH_2	14
				4.69d 4.21d	CH_2	14
				−11.83s	Os*H*	
				−12.17s	Os*H*	
$[Os_2(CO)_6(PhCH_2NCHNCH_2Ph)_2]$	2104w,	2080s,	2041s,	8.33s	NC*H*N	
(4)	1996vs,	1978m,	1961m	7.25m	C_6H_5	
				4.65d 4.31d	CH_2	14

$[\mathrm{Os_2(CO)_6(Pr^iNCHNPr^i)_2}]$ (5)	2076s, 1969m,	2036s, 1962m,	1989s, 1954s	8.33s	$\mathrm{NC}H\mathrm{N}$	
				2.64m	$CH\mathrm{Me_2}$	7
				1.12d	CH_3	7
$[\mathrm{Os_3H(CO)_9(PMe_2Ph)(Pr^iNCHNPr^i)}]$ [d] (6)	2088m, 2004m, 1961m,	2044m, 1990m, 1941mw	2011s, 1967mw,	3.71m	$CH\mathrm{Me_2}$	
				2.91m	$CH\mathrm{Me_2}$	
				2.02d	$\mathrm{P}CH_3$	10
				1.89d	$\mathrm{P}CH_3$	10
				1.01d	$\mathrm{CH}CH_3$	6
				0.94d	$\mathrm{CH}CH_3$	6
				0.75d	$\mathrm{CH}CH_3$	6
				0.24d	$\mathrm{CH}CH_3$	6
				−12.80d	$\mathrm{Os}H$	17
$[\mathrm{Os_3H(CO)_8(PMe_2Ph)(Pr^iNCHNPr^i)}]$ [e] (7)	2063m, 1984s, 1917w	2025m, 1955m,	2014m, 1941m,			
$[\mathrm{Os_3H_2(CO)_9(Pr^iNCHNPr^i)}]^+$ [f] (8)				9.30s	$\mathrm{NC}H\mathrm{N}$	
				3.81m	$CH\mathrm{Me_2}$	
				2.64m	$CH\mathrm{Me_2}$	
				1.36d	$\mathrm{CH(}CH_3\mathrm{)_2}$	7
				1.15d	$\mathrm{CH}CH_3$	7
				1.07d	$\mathrm{CH}CH_3$	7
				−12.30d	$\mathrm{Os}H$	2
				−13.78d	$\mathrm{Os}H$	2

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[a] In cyclohexane solution. [b] 100 MHz spectra in $\mathrm{CDCl_3}$ at 29°C. [c] 100 MHz spectrum in $\mathrm{CD_2Cl_2}$ at 29°C. [d] Benzene was used as lock signal so Ph and $\mathrm{NC}H\mathrm{N}$ signals were not observed. [e] Not isolated pure; NMR not recorded. [f] Formed by addition of $\mathrm{CF_3CO_2H}$ (0.05 cm^3) to a $\mathrm{CDCl_3}$ (0.50 cm^3) solution. Complex not isolated.

colourless compound identified as $[Os_2(CO)_6(PhCH_2NCHNCH_2Ph)_2]$ (**4**) was also obtained. The structure shown for **4** is consistent with spectra (see Table 1), notably the equivalence of the $PhCH_2$ groups and the diastereotopic CH_2 protons, and is also directly analogous to that established for $[Os_2(CO)_6(MeCO_2)_2]$ [13]. The analogy between *N,N*-dialkylformamidine and acetic acid is illustrated by the formation of related dinuclear compounds. The differences in ν(CO) frequencies, those for the N-compound being about 20—30 cm^{-1} lower than for the acetate, reflect the differing donor properties of these ligands.

Having found that eq. 1 does not operate when X = Y = NCH_2Ph because of *ortho*-metallation, we examined $Pr^iNHCH{=}NPr^i$ which is less likely to undergo cyclometallation at the Pr^i groups. Reaction of $[Os_3(CO)_{10}L_2]$ (L = cyclooctene) with the diisopropylformamidine unfortunately gave no isolable products. The direct reaction with $[Os_3(CO)_{12}]$ with $Pr^iNHCH{=}NPr^i$ in refluxing octane gave $[Os_3H(CO)_9(Pr^iNCHNPr^i)]$ (**2**), and after longer reaction times (9 h) small quantities of the dinuclear compound $[Os_2(CO)_6(Pr^iNCHNPr^i)_2]$ (**5**) were obtained. We were unable to obtain the direct analogue of **1** from these reactions. Compound **2** contains non-equivalent Pr^i groups over a wide range of temperatures (—60 to 133°C) with separate *C*HMe$_2$ multiplets (Table 1). Spectroscopically it is analogous to compound **11** (X = NH), the X-ray structure of which is known. One reason we wished to examine **2** was to see if μ_3-ligand rotation might lead to NMR coalescence effects. Rotation of the ligand with respect to the Os_3 triangle would interchange the "bridging" and "terminal" N atoms, alternating the two N—CH bonds after each 60° rotation. This assumes that the hydride ligand can migrate between Os—Os bonds in concert with the μ_3-ligand rotation. Lack of any coalescence rules this out. Two CH*Me*$_2$ doublets are observed at —60°C ($\Delta\delta$ 0.17 ppm) which steadily move together as the temperature is raised and a single doublet is obtained above 133°C. These observations result from changes in populations of conformers (rotation about the N—Pr^i bonds) and not to coalescence.

Protonation of compound **2** by addition of CF_3CO_2H to a $CDCl_3$ solution gave compound **8** which is similarly stereochemically rigid. As well as having non-equivalent Pr^i groups the CH*Me*$_2$ groups are now diastereotopic. Not only does the μ_3-ligand not rotate but there is also no hydride ligand migration. Crystalline samples of **8** could not be isolated but an oil was obtained on removal of the solvent which deprotonated in refluxing dichloromethane to regenerate compound **2**.

No reaction occurred when compound **2** was treated with CO (1 atm) at room temperature or when the gas was bubbled through a refluxing cyclohexane solution. However, addition of PMe_2Ph to **2** at room temperature gave the direct adduct **6** in excellent yield. ^1H NMR spectra are consistent only with the structure shown. What is very interesting is that this PMe_2Ph addition is reversed thermally! It is unusual for loss of PMe_2Ph to be favoured over that of CO. Only when N_2 was bubbled through a refluxing octane solution of **6** did loss of CO compete with loss of PMe_2Ph. Under these circumstances both **2** and $[Os_3H(CO)_8(PMe_2Ph)(Pr^iNCHNPr^i)]$ (**7**), were obtained. Unfortunately **7** could not be separated from **2** and could not be synthesised other than in a mixture with **2**.

Discussion

Chelating amidinato ligands are known in Group VI metal complexes [14—17]. For example, the formamidinato complexes $[Mo(C_5H_5)(CO)_2(RNCHNR)]$ formed from $[Mo(C_5H_5)(CO)_3Cl]$ are of this type [16]. Dinuclear complexes with μ_2-amidinato ligands like in compounds **4** and **5** are well known; again many are analogous to carboxylato complexes [18—21]. Group VI complexes of type $[M_2(\mu_2\text{-}RNCHNR)_4]$ have been known for a long time [18,21]. However, prior to this work there seems to have been no report of μ_3-amidinato complexes. Ligands which can donate differing numbers of electrons, like the formamidinato ligands donating three electrons in **1** but five electrons in **2** (with ligands as radicals), could have use in allowing the loss and uptake of ligands by clusters.

Experimental

The cyclooctene complex $[Os_3(CO)_{10}(C_8H_{14})_2]$ was prepared as reported [22], while *N,N*-diisopropyl and dibenzyl-formamidines were prepared by established methods [23].

Reaction of $[Os_3(CO)_{10}(C_8H_{14})_2]$ with N,N-dibenzylformamidine

A solution of the cyclooctene complex (0.280 g) in cyclooctene (20 cm^3) was mixed with a solution of $PhCH_2N{=}CHNHCH_2Ph$ (0.069 g) in dichloromethane (5 cm^3) and the mixture stirred under nitrogen for 80 min. Removal of solvent under vacuum gave a yellow oil which was separated by TLC (SiO_2) eluting with pentane to give several bands. One band gave $[Os_3H(CO)_{10}(PhCH_2NCHNCH_2Ph)]$ (**1**), as yellow crystals (0.044 g, 15%) from hexane solution at 0°C (Found: C, 28.7; H, 1.95; N, 2.4. $C_{25}H_{16}N_2O_{10}Os_3$ calcd.: C, 27.55; H, 1.55; N, 2.7%.) The other bands gave small amounts of uncharacterised materials.

Reaction of $[Os_3(CO)_{12}]$ with N,N-dibenzylformamidine

A bright yellow solution of $[Os_3(CO)_{12}]$ (0.297 g) and $PhCH_2N{=}CHNHCH_2Ph$ (0.131 g) in n-octane (50 cm^3) became very pale yellow after heating under reflux under nitrogen for 3 h. Some colourless crystals were formed when the solution was kept at —20°C and removal of the solvent under vacuum gave more. Purification of the combined solids by TLC (SiO_2), eluting with pentane/diethylether mixtures (1/1 by volume), gave $[Os_2(CO)_6(PhCH_2NCHNCH_2Ph)_2]$ (**4**), as colourless crystals (0.181 g, 37%) (Found: C, 43.7; H, 3.2; N, 5.45. $C_{36}H_{30}N_4O_6Os_2$ calcd.: C, 43.45; H, 3.05; N, 5.65%). Another chromatographic band gave $[Os_3H_2(CO)_9(C_6H_4CH_2NCHNCH_2Ph)]$ (**3**), (0.131 g, 36%) giving colourless crystals from hexane at 0°C (Found: C, 27.5; H, 1.8; N, 2.7. $C_{24}H_{16}N_2O_9Os_3$ calcd.: C, 27.55; H, 1.55; N, 2.7%).

Thermolysis of compound 1

A bright yellow solution of $[Os_3H(CO)_{10}(PhCH_2NCHNCH_2Ph)]$ (**1**), (0.133 g) in refluxing n-octane under nitrogen became pale yellow over 1 h. Removal of the solvent under vacuum gave a pale yellow solid which was purified by

TLC (SiO_2; eluant: diethylether) to give $[Os_3H_2(CO)_9(C_6H_4CH_2NCHNCH_2Ph)]$ (**3**), as a colourless solid (0.061 g, 47%). Although not apparent from the analytical data, compound **3** prepared in this way is contaminated with a trace of an unidentified yellow solid.

Reaction of compound **3** *with carbon monoxide*

Carbon monoxide (1 atm) was bubbled steadily through a solution of $[Os_3H_2(CO)_9(C_6H_4CH_2NCHNCH_2Ph)]$ (0.069 g) in refluxing octane (50 cm^3) for 4.25 h by which time the colourless solution had become yellow. Work-up involving chromatography on silica, eluting with pentane/CH_2Cl_2 (2/1 by volume), gave $[Os_3H(CO)_{10}(PhCH_2NCHNCH_2Ph)]$ (**1**), (0.026 g, 37%), starting material (0.025 g) and another yellow uncharacterised compound (0.006 g).

Reaction of $[Os_3(CO)_{10}(C_8H_{14})_2]$ with N,N'-diisopropylformamidine

In an attempt to prepare the analogue of compound **1**, the cyclooctene complex (0.140 g) was reacted at room temperature with $Pr^iN{=}CHNHPr^i$ (0.30 cm^3) in cyclooctene (10 cm^3) and dichloromethane (10 cm^3) for 2 days. The yellow product mixture was separated by TLC and gave several bands yielding no more than 0.009 g each, but none was identified and none analogous to compound **1**.

Reaction of $[Os_3(CO)_{12}]$ with N,N'-diisopropylformamidine

(a) A solution of $[Os_3(CO)_{12}]$ (0.365 g) with $Pr^iN{=}CHNHPr^i$ (0.30 cm^3) in n-octane (50 cm^3) was heated under reflux for 2.5 h. Removal of solvent and TLC (SiO_2) separation of the residue eluting with pentane/diethylether (1/1 by volume) gave $[Os_3H(CO)_9(Pr^iNCHNPr^i)]$ (**2**), as crystals (0.180 g) from hexane (Found: C, 20.65; H, 1.85; N, 2.95. $C_{16}H_{16}N_2O_9Os_3$ calcd.: C, 20.2; H, 1.7; N, 2.95%). Another band gave a solid mixture (0.124 g) which could not be separated.

(b) A similar treatment of $[Os_3(CO)_{12}]$ (0.285 g) with the formamidine (0.30 cm^3) in refluxing n-octane (50 cm^3) under nitrogen but for longer (9.25 h) resulted, after a similar work-up, in a colourless TLC band which gave $[Os_2(CO)_6(Pr^iNCHNPr^i)_2]$ (**5**), as colourless crystals (0.060 g, 16%) from hexane (Found: C, 30.25; H, 4.15; N, 7.1. $C_{20}H_{30}N_4O_6Os_2$ calcd.: C, 29.9; H, 3.75; N, 7.0%). Another band gave $[Os_3H(CO)_9(Pr^iNCHNPr^i)]$ (**2**), (0.154 g, 51%) contaminated very slightly with another unknown compound.

Reaction of compound **2** *with dimethylphenylphosphine*

PMe_2Ph (0.1 cm^3) was added to a solution of $[Os_3H(CO)_9(Pr^iNCHNPr^i)]$ (0.040 g) in dichloromethane (15 cm^3) and the mixture stirred at room temperature under nitrogen for 1 h. TLC work-up using SiO_2 eluting with pentane/diethyl ether (2/1 by volume) gave $[Os_3H(CO)_9(PMe_2Ph)(Pr^iNCHNPr^i)]$ (**6**), as yellow orange crystals (0.040 g, 87%) from CH_2Cl_2/hexane mixtures at 0° C (Found: C, 26.45; H, 2.8; N, 2.6. $C_{24}H_{27}N_2O_9Os_3P$ calcd.: C, 26.45; H, 2.5; N, 2.55%).

Thermolysis of compound (**6**)

A solution of $[Os_3H(CO)_9(PMe_2Ph)(Pr^iNCHNPr^i)]$ in refluxing octane was refluxed with N_2 passing through the solution for 3 h. Chromatography on silica eluting with pentane/diethyl ether (1/1 by volume) gave a single band as an inseparable mixture of $[Os_3H(CO)_9(Pr^iNCHNPr^i)]$ and $[Os_3H(CO)_8(PMe_2Ph)(Pr^iNCHNPr^i)]$ (ca. 1/1 mol ratio).

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