

OXIDATIVE ADDITION OF 2-FORMYL-FURAN AND RELATED PYRROLE AND THIOPHENE COMPOUNDS AT TRIOSMIUM CLUSTERS

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Summary

The bridging acyl complexes $[\text{Os}_3\text{H}(\mu\text{-COC}_4\text{H}_3\text{X})(\text{CO})_{10}]$ ($\text{X} = \text{NH}$, O , or S) have been prepared by oxidative addition of the 2-formyl derivatives of pyrrole, furan, or thiophene ($\text{C}_4\text{H}_3\text{XCHO}$) at $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ with cleavage of the aldehydic C–H bonds. On heating double decarbonylation of the acyl complexes occurs, to afford high yields of the compounds $[\text{Os}_3\text{H}_2(\text{CO})_9(\mu_3\text{-C}_4\text{H}_2\text{X})]$, reported previously for $\text{X} = \text{NH}$ or O . For $\text{X} = \text{NH}$, two isomers with this formulation were characterised by ^1H NMR and IR data; the one containing the $\mu_3\text{-2,3-C}_4\text{H}_3\text{N}$ ligand isomerises to one containing $\mu_3\text{-1,2-C}_4\text{H}_3\text{N}$. The direct reaction of pyrrole with $[\text{Os}_3(\text{CO})_{12}]$ has been re-examined at lower temperatures than before, and observed to give new products, including $[\text{Os}_3\text{H}(\text{CO})_{10}(\text{C}_4\text{H}_4\text{N})]$, which contains a bridging non-aromatic tautomeric form of pyrrole. The ability of Os_3 clusters to stabilize non-aromatic tautomers of aromatic ligands is discussed.

Introduction

We have been interested in the reactions of α,β -unsaturated aldehydes with triosmium clusters because oxidative addition can occur with C–H cleavage either at the formyl or the alkenyl group [1]. In the former case μ -acyl complexes are generated. 2-Formyl-pyrrole, -furan, or -thiophene might be regarded as α,β -unsaturated aldehydes, so that oxidative addition could occur at the CHO group or at the ring. Previously it has been shown that oxidative addition of the ring C–H bonds occurs for pyrrole [2] and furan [3] to give triosmium clusters.

Results and discussion

Scheme 1 shows the reactions of the aldehydes with $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$. In the case of the pyrrole and furan derivatives only products **1** (66%) and **2** (60%), formed

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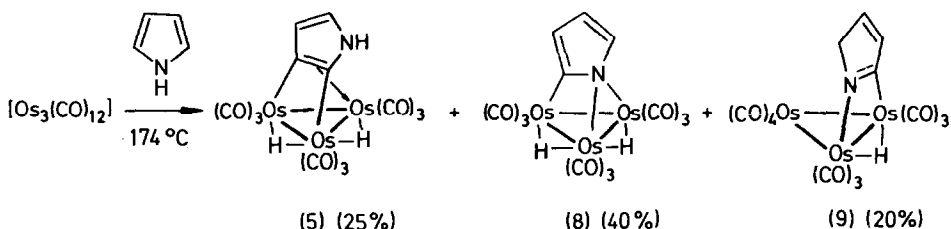
TABLE 1
SOME SPECTROSCOPIC DATA FOR COMPOUNDS 1-10

Compound	$\nu(\text{CO})^a$ (cm^{-1}) Terminal carbonyl ligands	$\nu(\text{CO})^b$ (cm^{-1}) Acyl ligands	$^1\text{H NMR}^c$
$[\text{Os}_3\text{H}(\text{CO})_{10}(\text{HNCH}^x=\text{CH}^y\text{CH}^z=\text{CCO})]^d$ (1)	2104m, 2066vs, 2056s, 2028vs, 2016s, 2010sh, 1983m	1425 /	NH z x y OsH x y z OsH x,z y OsH z y x OsH NH y x OsH ₂ OsH ₂
$[\text{Os}_3\text{H}(\text{CO})_{10}(\text{OCH}^x=\text{CH}^y\text{CH}^z=\text{CCO})]^d$ (2)	2100m, 2062vs, 2052s, 2022vs, 2010s, 2006sh, 1990m, 1974m,	1430	8.90br 7.20m 7.00m 6.30m -13.0s 8.14d 6.78dd 7.34d -13.6s
$[\text{Os}_3\text{H}(\text{CO})_{10}(\text{SCH}^x=\text{CH}^y\text{CH}^z=\text{CCO})]^e$ (3)	2106m, 2065vs, 2054s, 2023vs, 2014vs, 2009sh, 1995m	1435	7.81m 7.14dd -13.6s
$[\text{Os}_3\text{H}(\text{CO})_{10}(\text{SCH}^x=\text{CH}^y\text{C}=\text{CCH}^z\text{O})]^e$ (4)	2122m, 2069s, 2049s, 2021vs, 2008s, 1980m, 1938m,	1445	9.15d 8.07d 7.51dd -15.0s
$[\text{Os}_3\text{H}_2(\text{CO})_9(\text{HNCCCH}^x=\text{CH}^y)]^e$ (5)	2105m, 2075vs, 2050vs, 2027vs, 2022sh, 2008vs, 1991m, 1978m, 1950vw	^h	8.60br 7.16dd 6.70dd -18.9s -16.7br -21.1br

J_{xz} 1.2
 J_{yz} 4.0
 J_{xy} 1.6
 $J_y(\text{NH})$ 2.4^g
 $J_z(\text{NH})$ 2.5^g
 J_{xy} 1.7
 J_{yz} 3.7
 J_{xz} 0.7
 J_{xy} 4.0
 J_{yz} 4.0
 J_{xy} 4.7
 J_{xz} 0.5
 J_{xy} 3.1
 $J_x(\text{NH})$ 1.3^g
 $J_y(\text{NH})$ 1.7^g
 $J_y(\text{NH})$ (30°C)
(-85°C)

[Os ₃ H ₂ (CO) ₉ (OC=CCH ^x =CH ^y)] ^e (6)	2108m, 2084vs, 2058vs, 2036vs, 2028s, 2010s, 2000m, 1992m, 1977w	7.80d	x	J _{x,y}	2.0
		7.00d			
[Os ₃ H ₂ (CO) ₉ (SC=CCH ^x =CH ^y)] ^e (7)	2108m, 2081vs, 2054vs, 2033vs, 2024s, 2008vs, 1999s, 1985m, 1973mw, 1958w	-19.4s	y	OsH ₂	(35 °C)
		-17.4br			
		-21.5br			
		7.44d			
[Os ₃ H ₂ (CO) ₉ (NCH ^x =CH ^y CH ^z =C)] ^{e,f} (8)	2105m, 2080vs, 2050vs, 2027sh, 2025vs, 2005vs, 1997m, 1978m	7.29d	x	J _{x,y}	5.1
		-19.2s			
		-18.3br			
		-20.2br			
[Os ₃ H(CO) ₁₀ (N=CCH ^x =CH ^y CH ^z)] ^e (9)	2102m, 2060vs, 2050s, 2020vs, 2006m, 2001m, 1993m, 1980w	7.50dd	z ^g	J _{x,y}	4.3
		7.40dd			
		6.62dd			
		-16.3s			
[Os ₃ H ₂ (CO) ₉ (MeNC=CCH ^x =CH ^y)] ^e (10)	2104m, 2074vs, 2048vs, 2025vs, 2022sh, 1998vs, 1989m, 1976m, 1945w	-15.6d	x	J _{x,y}	5.3
		-17.1d			
		7.04dt			
		6.60dt			
		4.70br	y	J _{x,z}	0.7
		-15.2s			
		7.06d			
		6.66d			
		3.60s	z	J _{y,z}	1.7
		-18.8s			
		-17.0br			
		-21.1br			
		7.06d	x	J _{x,y}	3.6
		6.66d			
		3.60s			
		-18.8s			
		-17.0br	y	NMe	(27 °C)
		-21.1br			
		OsH ₂			
		OsH ₂			
		-17.0br	z	OsH	(-80 °C)
		-21.1br			
		OsH ₂			
		OsH ₂			

^a Cyclohexane solutions. ^b Fluorolube mulls. ^c 100 MHz at room temperature; chemical shifts δ (ppm); J (Hz). ^d (CD₃)₂CO solution. ^e CDCl₃ solution. ^f ν (NH) 3464 cm⁻¹. ^g Coupling not well resolved in H^z signal. ^h ν (NH) 3450 cm⁻¹. ⁱ This compound was originally reported [2] as compound 5 but is now reformulated.



SCHEME 3

(around 190°C) [2]. We have re-examined these compounds and have found that compound **5** as reported here is directly comparable with compounds **6** and **7**, and that the compound we originally and incorrectly described as **5** [2] is actually an isomer which we now formulate as compound **8**. Indeed in the decarbonylation of **1** both isomers **5** and **8** are obtained. Compound **6** was reported earlier to be formed by decarbonylation of $[\text{Os}_3\text{H}(\mu_2\text{-C}_4\text{H}_3\text{O})(\text{CO})_{10}]$, itself formed from furan [3]. This is the first report of the thiophene-2,3-diyl compound **7**, and it is perhaps surprising that this is formed rather than any compound containing Os–S bonds in view of the proliferation of such compounds [8].

In our initial report on the products of the reaction of $[\text{Os}_3(\text{CO})_{12}]$ and pyrrole and *N*-methylpyrrole we commented upon the differences between the two derivatives $[\text{Os}_3\text{H}(\text{CO})_9(\mu_3\text{-C}_4\text{H}_2\text{NR})]$ ($\text{R} = \text{H}$ or Me) that were isolated [2]. Compound **10** when $\text{R} = \text{Me}$ can now be seen to be spectroscopically entirely analogous to compounds **5** to **7**, and different from the species we originally reported with $\text{R} = \text{H}$. When there is an *NH* atom, the initially formed compound **5** isomerises by transfer of this hydrogen atom to carbon to give the more stable isomer **8**. Carrying out the reaction of pyrrole with $[\text{Os}_3(\text{CO})_{12}]$ at temperatures below 190°C gave a mixture of isomers **5** and **8** and other products (Scheme 3; see later).

The formulation of cluster **8** as the N,C-bonded form is based on ^1H NMR and IR data. The originally reported $\nu(\text{NH})$ absorptions for **8** at 3670 and 3600 cm^{-1} are spurious. These absorptions were found for Nujol mulls but completely pure samples give no $\nu(\text{NH})$ absorptions in this region, whereas isomer **5** shows an absorption at 3450 cm^{-1} , close to that found for compound **1** (3464 cm^{-1}). The ^1H NMR signal originally reported for *NH* at δ 7.50 ppm can with hindsight be seen to be too sharp for such a resonance, and is now assigned to *CH* (see Table 1). Isomer **8** gives $^{13}\text{C}\{^1\text{H}\}$ NMR signals for the *CH* atoms at δ 117.2, 149.3, and 167.8 ppm (3-, 4-, and 5-positions) and a weak absorption at δ 175.9 ppm (2-position).

We have examined the conversion of isomer **5** into isomer **8**. Treatment of isomer **5** with $\text{D}_2\text{O}/\text{CDCl}_3$ caused a very slow exchange of the *NH* proton over many hours, but upon addition of catalytic quantities of NEt_3 the exchange was complete within 2–3 min at room temperature, that is within the time required to record a ^1H NMR spectrum. Figure 1 shows the NMR spectra confirming this exchange. On standing a solution of $[\text{Os}_3\text{H}_2(\text{CO})_9(\text{C}_4\text{H}_2\text{ND})]$ (**5**) (still containing an excess of D_2O) is slowly converted into $[\text{Os}_3\text{HD}(\text{CO})_9(\text{C}_4\text{H}_3\text{N})]$, isomer **8**. Thus the H-atom transfer to carbon is from osmium and not nitrogen. Various mechanisms are possible, but not an intraligand H-atom transfer. We have formulated compound **8** in Scheme 2 with bridging nitrogen, but we cannot yet actually distinguish this from

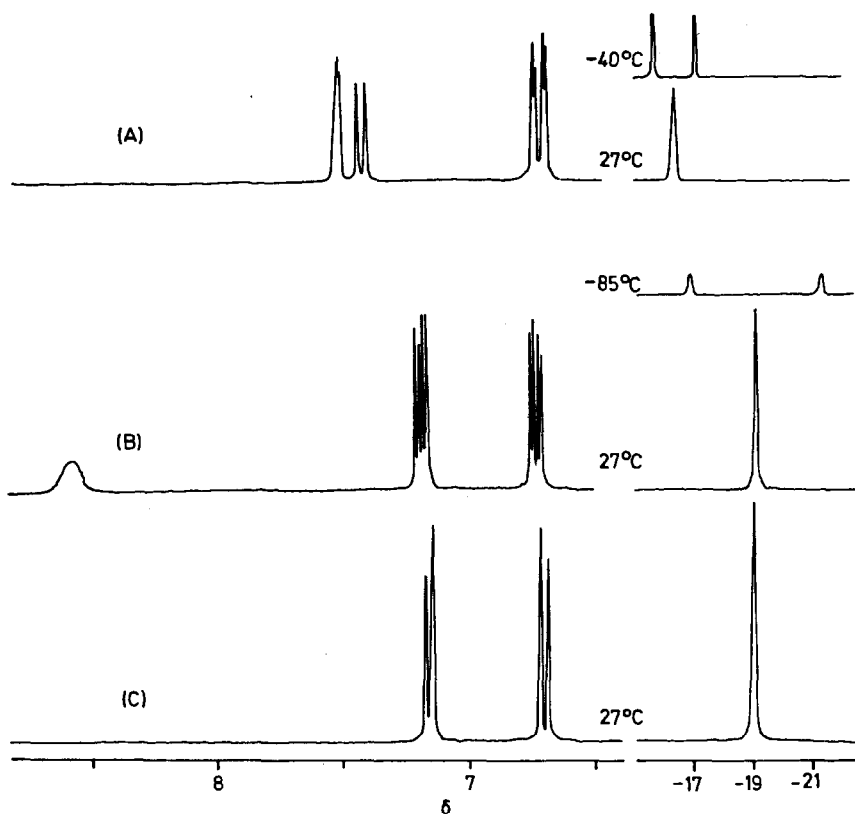
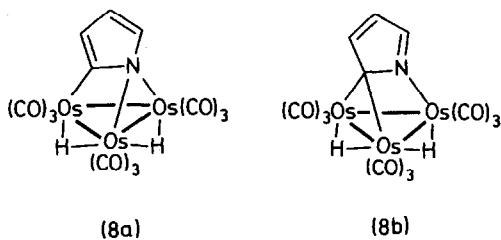
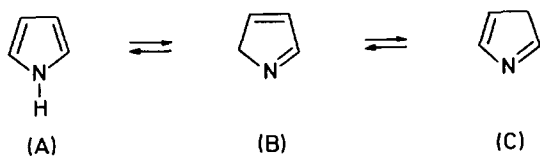


Fig. 1. ^1H NMR spectra of CDCl_3 solutions of (A) cluster **8** $[\text{Os}_3\text{H}_2(\text{C}_4\text{H}_3\text{N})(\text{CO})_9]$, (B) cluster **5** $[\text{Os}_3\text{H}_2(\text{C}_4\text{H}_2\text{NH})(\text{CO})_9]$, and (C) cluster **5** after treatment of a CDCl_3 solution with D_2O and Et_3N (catalytic amounts).

a carbon-bridged form. We are trying to grow good crystals for an X-ray structural determination in order to distinguish between forms **8a** and **8b**.



The other product from the reaction of pyrrole with $[\text{Os}_3(\text{CO})_{12}]$ at 174°C is compound **9**, $[\text{Os}_3\text{H}(\text{CO})_{10}(\text{C}_4\text{H}_4\text{N})]$. As with **8**, compound **9** is bonded through nitrogen. The IR spectrum near 2000 cm^{-1} is almost indistinguishable from that of the 2-pyridyl compound $[\text{Os}_3\text{H}(\text{CO})_{10}(\text{C}_5\text{H}_4\text{N})]$ and other 2-metallated nitrogen heterocycles [9], and this confirms the N,C-mode of attachment. The ^1H NMR spectrum (Table 1) confirms the non-aromatic form of the ligand. Indeed, in compound **9** an unstable tautomer of free pyrrole has been stabilised (see Scheme 4). The two non-aromatic forms, **B** and **C**, without N-H bonds, are clearly unstable



SCHEME 4

with respect to A. We believe we have trapped form B in compound 9 with the CH₂ group adjacent to nitrogen on the basis of the ¹H NMR shift for the CH₂ protons which are accidentally isochronous. In both compounds 8 and 9 non-aromatic forms of the ligand are stabilized, the loss of aromaticity being compensated for by the formation of N–Os bonds. The stabilization of the cyclohexadienone form of phenol by the triosmium cluster has previously been described, and this is mainly a consequence of forming strong σ-bonds between osmium and the μ₃-ligand.

Experimental

2-Formylfuran (2-furaldehyde), 2-formylpyrrole (2-pyrrolaldehyde), and 2-formylthiophene (2-thiophenaldehyde) were synthesised by literature methods or purchased from Aldrich. [Os₃(CO)₁₀(MeCN)₂] was synthesised as described earlier [1].

Reaction of [Os₃(CO)₁₀(MeCN)₂]

2-Formylfuran. A solution of [Os₃(CO)₁₀(MeCN)₂] (0.300 g) and freshly purified C₅H₄O₂ (1 cm³) in LiAlH₄-dried cyclohexane (50 cm³) was heated under reflux under N₂ for 4 h. Removal of the solvent under vacuum and separation of the residue by TLC (SiO₂, eluant, n-hexane) gave four bands. The main yellow band gave [Os₃H(CO)₁₀(μ-OCH=CHCH=CCO)] (2), as yellow crystals (0.180 g, 60%), and another band gave [Os₃H₂(CO)₁₀] as purple crystals (0.030 g, 10%). The other two bands only gave traces of compounds which were not characterised.

2-Formylpyrrole. A solution of [Os₃(CO)₁₀(MeCN)₂] (0.350 g) and C₅H₅ON (0.30 g) in dried cyclohexane (40 cm³) was heated under reflux for 3 h under nitrogen. The brown residue after removal of solvent under vacuum was separated by TLC (SiO₂; eluant, pentane) and gave four bands of which only one gave any significant amount of material which was characterised as [Os₃H(CO)₁₀(μ-HNCH=CHCH=CCO)] (1), as yellow crystals (0.200 g, 66%).

2-Formylthiophene. A solution of [Os₃(CO)₁₀(MeCN)₂] (0.250 g) and freshly distilled C₅H₄OS (2 cm³) in dried cyclohexane (30 cm³) was heated under reflux under N₂ for 2 h. The orange-yellow residue after removal of solvent was separated by TLC [SiO₂; eluant, petroleum ether (b.p. 40–60°C)] to give only two bands. The main one gave [Os₃H(CO)₁₀(μ-SCH=CHCH=CCO)] (3), as yellow crystals (0.080 g, 40%) and [Os₃H(CO)₁₀(SCH=CHC=CHO)] (4), as yellow crystals (0.060 g, 30%).

Reaction of [Os₃(CO)₁₂] with pyrrole

The reaction previously carried out in refluxing decalin [2] was repeated at somewhat lower temperatures. A solution of [Os₃(CO)₁₂] (0.200 g) and pyrrole (3 cm³) in n-decane (50 cm³) was heated under reflux for 4 h. Removal of the solvent

under vacuum and TLC separation (SiO_2 ; eluant, petroleum ether (b.p. 40–60°C)) gave four bands yielding: $[\text{Os}_3\text{H}_2(\text{CO})_9(\mu_3\text{-}\overline{\text{NCH=CHCH=C}})]$ (**8**), as yellow crystals (0.080 g, 40%) the isomeric form of this $[\text{Os}_3\text{H}_2(\text{CO})_9(\mu_3\text{-}\overline{\text{NH=CCCH=CH}})]$ (**5**), as pale yellow crystals (0.050, 25%), $[\text{Os}_3\text{H}(\text{CO})_{10}(\mu\text{-}\overline{\text{N=CCH=CHCH}_2})]$ (**9**), as yellow crystals (0.040 g, 20%), and a trace of $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$.

Thermolysis of acyl compounds 1–3

Compound 1. A solution of $[\text{Os}_3\text{H}(\text{CO})_{10}(\overline{\text{HNCH=CHCH=CCO}})]$ (0.200 g) in n-decane (50 cm^3) was heated under reflux for 15 min. Removal of solvent under vacuum and TLC separation (SiO_2 , eluant: petroleum ether (b.p. 40–60°C)) gave two main yellow bands yielding $[\text{Os}_3\text{H}_2(\text{CO})_9(\overline{\text{NCH=CHCH=C}})]$ (**8**), (0.080 g, 40%) and its isomer (**5**), (0.060 g, 30%) both as yellow crystals. Using rather lower temperatures (refluxing n-octane) gave mainly compound **5** (65%).

Compound 2. A solution of $[\text{Os}_3\text{H}(\text{CO})_{10}(\overline{\text{OCH=CHCH=CCO}})]$ (0.150 g) in octane (30 cm^3) was heated under reflux for 4 h. Removal of the solvent under vacuum and TLC separation as above gave several minor bands which were uncharacterised and one main yellow one which yielded $[\text{Os}_3\text{H}_2(\text{CO})_9(\overline{\text{OC=CCH=CH}})]$ (**6**), as yellow crystals (0.060 g, 40%) which was characterised by comparison with published spectroscopic data for this compound [3].

Compound 3. A solution of $[\text{Os}_3\text{H}(\text{CO})_{10}(\overline{\text{SCH=CHCH=CCO}})]$ (0.125 g) in cyclohexane (50 cm^3) was heated under reflux for 15 h and subsequent work-up as above gave two main species: $[\text{Os}_3\text{H}_2(\text{CO})_9(\overline{\text{SC=CCH=CH}})]$ (**7**) as yellow crystals (0.062 g, 50%) and recovered **3** (0.031 g, 25%).

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