Pergamon

Polyhedron Vol. 16, No. 21, pp. 3775–3778, 1997
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0277–5387/97 $17.00 + 0.00

PII: S0277–5387(97)00145–9

Polynuclear carbonyl clusters containing heterocyclic hydrocarbons. The synthesis and X-ray crystal structure of $[Os_3H(CO)_9(NMe_3)(\mu\text{-}COC_4H_4N)]$ $\{\mu\text{-}CONC_4H_4 = \text{2-acylpyrrole}\}$

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(Received 20 February 1997; accepted 11 April 1997)

Abstract—The reaction between the acyl-substituted triosmium cluster $[Os_3H(CO)_{10}(\mu\text{-}COC_4H_4N)]$ and trimethylamine-N-oxide, at $-78°C$, yields not the expected pyrrole-linked cluster but the novel trimethylamine complex $[Os_3H(CO)_9(NMe_3)(\mu\text{-}COC_4H_4N)]$ (**1**). An X-ray crystal structure of the product shows that it consists of an η^2-2-acylpyrrole bridged triosmium unit incorporating a terminally coordinated trimethylamine ligand which occupies an equatorial site on the osmium triangle. © 1997 Elsevier Science Ltd

Keywords: osmium; pyrrole; cluster carbonyl; acyl; trimethylamine; X-ray crystal structure.

The chemistry of trinuclear metal carbonyl clusters coordinating pyrrole ligands is well documented [1,2]. Pyrrole is isoelectronic with the cyclopentadienyl anion and differs only in the replacement of an sp^2 hybridised carbon atom with a similarly hybridised nitrogen atom. However, the presence of the ring nitrogen atom significantly alters the reactivity of the pyrrole ring by comparison with the cyclopentadienyl ligand. The chemical and physical properties of the pyrrole molecule do, however, fulfil all of the qualitative criteria generally accepted for aromaticity [3]. Pyrrole adopts a wide range of bonding modes in both mono- and polynuclear complexes [4], however, structurally characterised η^5-coordinated pyrrole compounds are rare, existing only for mononuclear complexes [5–9]. Few polynuclear pyrrole complexes exist, and these tend to incorporate orthometallated pyrrole ligands in which C—H and/or N—H scission has occurred to yield an η^2-ligand bridged complex [1]. The previously reported cluster $[Os_3H(CO)_{10}(\mu\text{-}COC_4H_4N)]$ [2], in which the pendant pyrrole molecule is anchored but not directly coordinated to the triosmium decacarbonyl cluster by an acyl interaction has been utilised for its potential to produce some form of chemically induced π-interaction of the ring and metal unit. However, in this paper we report the synthesis and characterisation of a novel triosmium cluster, containing the pyrrole ligand, in which the reagent used to activate the cluster has been coordinated in preference to the pendant pyrrole ligand.

RESULTS AND DISCUSSION

The title complex is prepared by the direct reaction of $[Os_3H(CO)_{10}(\mu\text{-}COC_4H_4N)]$ and trimethylamine-N-oxide, in dichloromethane, at $-78°C$ for 1 h (Scheme 1). The complex $[Os_3H(CO)_9(NMe_3)(\mu\text{-}COC_4H_4N)]$ (**1**) was initially characterised by spectroscopic techniques. The ^1H and ^{13}C NMR spectra of the cluster show signals corresponding to the pyrrole ring that are very similar to those observed in the parent cluster [2], and that coordination to the metal framework has not occurred. The acyl functionality is also observed in the ^{13}C NMR spectrum, with the signal for the acyl carbon atom at δ 234. Nine discrete carbonyl resonances are also observed in the ^{13}C NMR spectrum indicating that the molecule is static on the NMR time scale at 25°C. The ^1H NMR spectrum also displayed a singlet signal at δ 3.00 and the ^{13}C NMR spectrum displayed a resonance at δ 59.7, both of which correspond to the presence of methyl groups.

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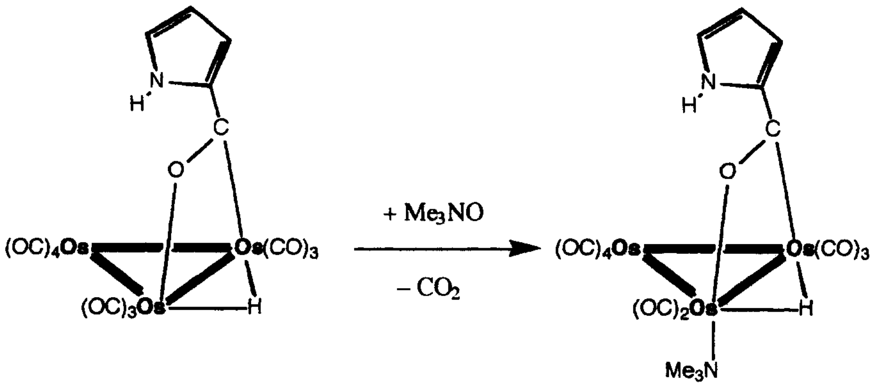

Scheme 1. The reaction leading to the formation of 1.

In order to establish the exact nature of the product (**1**) a single crystal X-ray analysis was undertaken. The molecular structure of (**1**) is shown in Fig. 1 while selected bond parameters are listed in Table 1. The metal framework consists of a scalene osmium triangle with the (μ-COC_4H_4N) group lying almost perpendicular to the Os_3 plane. The nine carbonyls are all terminal and essentially linear. The hydride was not directly located but potential energy calculations [10] indicate that it bridges the Os(1)—Os(2) edge. In this coordination mode the acylpyrrole ligand acts as a three electron donor, donating two electrons through the σ-oxygen interaction and one electron through the σ-carbon interaction. A trimethylamine ligand, derived from the trimethylamine-N-oxide molecule that was used to activate the parent cluster through oxidation of a terminal carbonyl ligand, is σ-bound to Os(1) and occupies an equatorial site. The specificity of attack at this site is presumably related to the electron donating properties of the acyl group, with the trimethylamine ligand bound to the same osmium as the two electron-donating oxygen atom. In terms of electron counting, the cluster has 48 electrons, which is consistent with the *closed* triangular metal framework.

The molecular dimensions of (**1**) follow similar trends to those observed in the parent complex [$Os_3H(CO)_{10}(\mu$-$COC_4H_4N)$] [11]. The C—O bond length in the acyl ligand is 1.24(2) Å, characteristic of an η^2-acyl. The Os(1)–carbon distances to the carbonyl ligands are substantially shorter than those at the other osmium centres. The delocalised pyrrole ring and the acyl group are coplanar and the C(1)—C(2) bond length is 1.46(2) Å, substantially shorter than the expected C—C single bond distance indicating a degree of delocalisation between the pyrrole ring and the acyl functionality.

The presence of a coordinated trimethylamine ligand in cluster chemistry is uncommon despite the fact that trimethylamine-N-oxide is used extensively to activate carbonyl ligands by oxidising the coordinated carbonyl to carbon dioxide. The vacant coordination site generated by this process is usually filled by an incoming nucleophile. In this case, the geometric constraints on the pyrrole ring prevent any interaction with the osmium framework, and the only available nucleophile is the NMe_3 generated in the oxidation process. The Os(1)—N(1) bond is relatively long, at 2.282(13) Å, suggesting that the interaction is weak. This distance is comparable with the Os—N distance of 2.22(2) Å found for the Os—NMe_3 bond in [$Os_3(CO)_9(NO)_2(NMe_3)$] [12] where the trimethylamine group also occupies an equatorial position on an osmium triangle.

Attempts to remove the NMe_3 ligand by thermolysis have proved unsuccessful until the reaction temperature (refluxing octane) results in extensive bond cleavage and the production of the known orthometallated pyrrole complex [$Os_3H_2(CO)_9(\mu_3$-$(\eta^2$-$\|)$ $NC_4H_3)$] [11].

EXPERIMENTAL

All the reactions were performed using standard Schlenk techniques under an atmosphere of dry, oxygen-free nitrogen. Technical grade solvents were purified by standard procedures. The complex [$Os_3H(CO)_{10}(\mu$-$COC_4H_4N)$] was prepared by the literature procedure [2]. Me_3NO was used as supplied, without further purification. Infrared spectra were recorded as dichloromethane solutions in a NaCl cell (0.5 mm path length) on a Perkin–Elmer 1710 Fourier Transform spectrometer. FAB mass spectra were recorded on an AE1/Kratos MS 50 spectrometer. NMR spectra were recorded on a Bruker AM 400 Fourier Transform spectrometer in appropriate solvents. The chemical shifts were referenced to residual protons in CD_2Cl_2 (7.25 ppm) for ^1H and (53.3 ppm) for ^{13}C nuclei.

Preparation of [$Os_3H(CO)_9(NMe_3)(\mu$-$COC_4H_4N)$] (**1**)

[$Os_3H(CO)_{10}(\mu$-$COC_4H_4N)$] (50 mg, 0.051 mmol) was dissolved and magnetically stirred in CH_2Cl_2 at -78°C. Me_3NO (4 mg, 0.052 mmol) was added to the

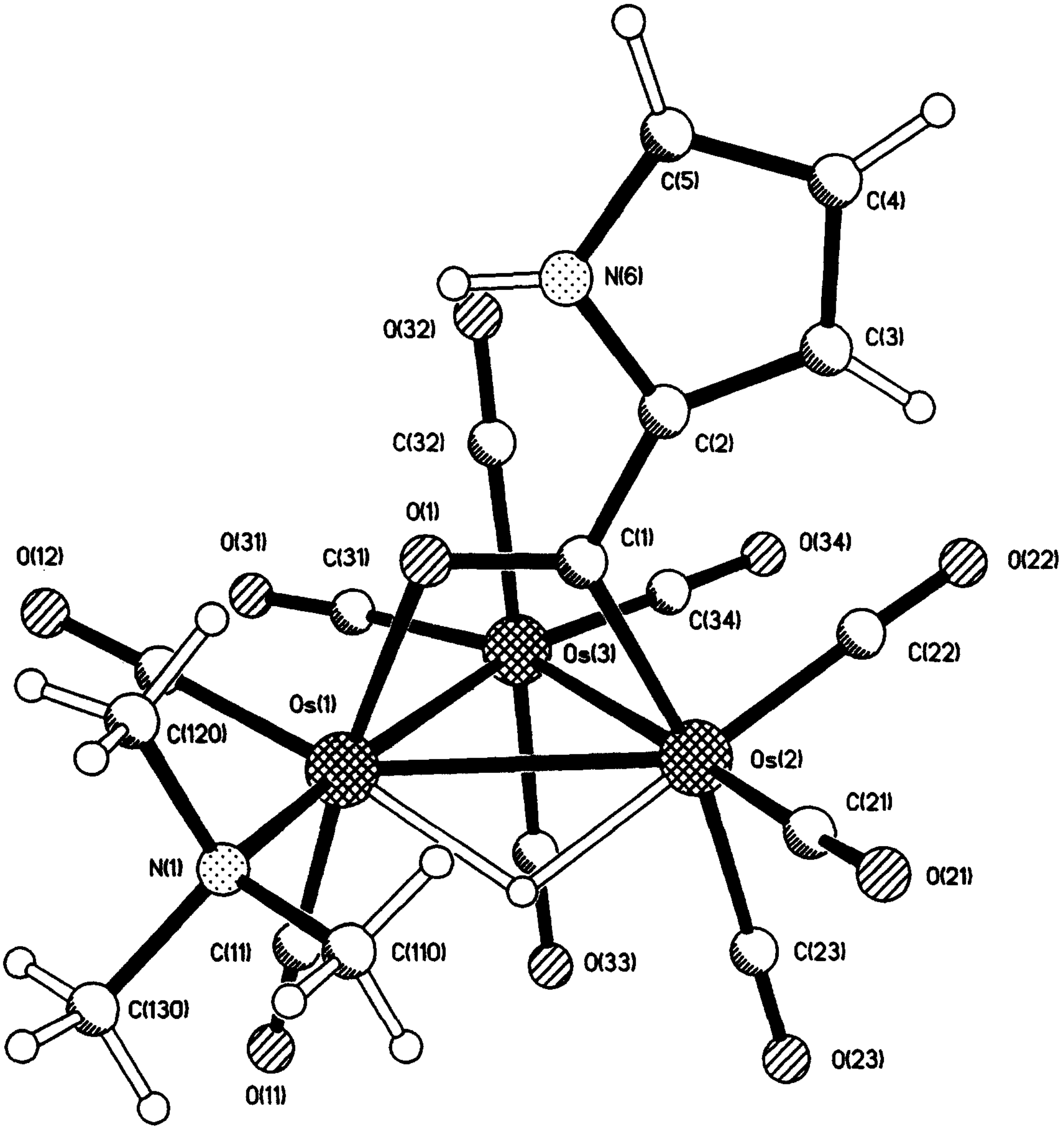

Fig. 1. The molecular structure of (**1**) showing the atom numbering scheme.

Table 1. Selected bond lengths (Å) and angles (°) for [$Os_3H(CO)_9(NMe_3)(\mu\text{-}COC_4H_4N)$] (**1**)

Os(1)—Os(2)	2.9339(9)	Os(1)—Os(3)	2.8208(9)
Os(2)—Os(3)	2.8851(10)	Os(2)—C(1)	2.087(13)
Os(1)—O(1)	2.157(10)	C(1)—O(1)	1.24(2)
N(1)—Os(1)	2.282(13)	C(1)—C(2)	1.46(2)
C(2)—C(3)	1.36(2)	C(3)—C(4)	1.37(3)
C(4)—C(5)	1.36(3)	C(5)—N(6)	1.36(2)
Os(1)—C(12)	1.85(2)	Os(1)—C(11)	1.88(2)
Os(2)—C(21)	1.95(2)	Os(2)—C(22)	1.87(2)
Os(2)—C(23)	1.97(2)	Os(3)—C(31)	1.86(2)
Os(3)—C(32)	1.96(2)	Os(3)—C(33)	1.93(2)
Os(3)—C(34)	1.91(2)		

Os(3)—Os(2)—Os(1)	57.98(2)	Os(1)—Os(3)—Os(2)	61.87(2)
Os(3)—Os(1)—Os(2)	60.14(2)	Os(2)—C(1)—C(2)	126.5(11)
Os(2)—C(1)—O(1)	119.1(12)	C(1)—Os(2)—Os(3)	86.0(4)
O(1)—C(1)—C(2)	114.4(13)		

solution and a colour change from orange to lemon yellow was observed over 0.5 h. The mixture was stirred for 1 h and allowed to slowly come to room temperature. The resulting yellow CH_2Cl_2 solution was evaporated to dryness under reduced pressure. The resulting powdery solid was redissolved in a minimum of CH_2Cl_2 (2 ml) and was purified by thin layer chromatography (silica gel), eluting with CH_2Cl_2 (10%)/hexane (90%), affording (**1**) as a bright yellow air stable solid. (**1**) was recrystallised from CH_2Cl_2/hexane, affording yellow blocks (yield 95%). IR (CH_2Cl_2): [cm^{-1}] = 2091(m), 2049(vs), 2011(vs), 1992(s), 1974(m), 1965(sh), 1918(m) MS (-FAB): *m/z*: 976. ^1H NMR (250 MHz, CD_2Cl_2): $\delta = 9.20$ (s{broad}), 1H, N*H*), 7.28 (m, 1H, C*H*), 7.16 (m, 1H, C*H*), 6.39 (m, 1H, C*H*), 3.00 (s, 9H, N*Me*$_3$), -14.35 (s, 1H, Os*H*Os). $^{13}C\{^1H\}$ NMR (250 MHz, CD_2Cl_2): $\delta = 233.9$ (s, 1C; acyl *C*), 185.60 (s, 1C, CO), 185.38 (s, 1C, *C*O), 182.36 (s, 1C, *C*O), 180.27 (s, 1C, *C*O), 179.25 (s, 1C, *C*O), 178.27 (s, 1C, *C*O), 176.59 (s, 1C, *C*O), 174.77 (s, 1C, *C*O), 174.07 (s, 1C, *C*O), 144.51 (s, 1C, pyrrole *C*), 125.43 (s, 1C, pyrrole *C*), 123.43 (s, 1C, pyrrole *C*), 112.03 (s, 1C, pyrrole *C*), 59.17 (s, 3C, N*Me*$_3$). Elemental anal.: Found (calc.) C 20.51 (20.80); H 1.27 (1.40); N 2.84 (2.84).

X-ray crystal structure determination of $[Os_3H(CO)_9(NMe_3)(\mu\text{-}COC_4H_4N)]$ (**1**)

The general operating procedures have been described previously [13].

Crystal data for $[Os_3H(CO)_9(NMe_3)(\mu\text{-}COC_4H_4N)]$ (**1**): $C_{17}H_{14}N_2O_{10}Os_3$, $M = 976.90$, monoclinic, space group $P2_1/c$, $a = 14.408(2)$, $b = 16.570(3)$, $c = 9.7140(10)$ Å, $\beta = 94.750(10)°$, $U = 2311.2(6)$ Å^3, $T = 293(2)$ K, graphite-monochromated Mo–K_α radiation, $\lambda = 0.71073$ Å, $Z = 4$, $D_c = 2.808$ Mg m^{-3}, $F(000) = 1752$, yellow block, $0.35 \times 0.12 \times 0.09$ mm, μ(Mo-K_α) = 16.506 mm^{-1}, semi-empirical absorption correction based on ψ-scans, transmission factors 0.094–0.285, Stoe-Siemens AED four-circle diffractometer, data collection range $7.2 < 2\theta < 45.0°$, $\pm h$, $\pm k$, $\pm l$, 3 standard reflections showed no significant variation in intensity. 6018 reflections, 3013 unique ($R_{int} = 0.0382$) used in all calculations.

The structure was solved by direct methods (SHELXTL PLUS) [14] and subsequent Fourier syntheses, and refined by full-matrix least squares on F^2 (SHELXL-93) [15] with all non-hydrogen atoms assigned anisotropic displacement parameters. Hydrogen atoms were included using a riding model. Final residuals were $wR(F^2)$ 0.154 on all data, conventional $R(F)$ 0.056 for 2593 observed reflections [$I > 2\sigma(I)$], weighting scheme $w = 1/[\sigma^2(F_0) + (0.118P)^2 + 7.11P]$ where $P = (F_0^2 + 2F_c^2)/3$, 293 parameters, g.o.f. = 1.033, maximum $\Delta/\sigma = 0.001$, maximum Δ/ρ 2.99, minimum -2.77 e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements—We thank the E.P.S.R.C. (to L.P.C. and G.P.S.) and the Cambridge Crystallographic Data Centre (to G.P.S.) for financial support. We are grateful to Johnson Matthey for the generous loan of osmium tetroxide.

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