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Substitution derivatives of the heteronuclear cluster $RuOs_3(\mu\text{-}H)_2(CO)_{13}$: Disubstituted group 15 derivatives

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Abstract

The structures in the solid state and solution state of tertiary group 15 ligand disubstituted derivatives of the heteronuclear cluster $RuOs_3(\mu\text{-}H)_2(CO)_{13}$ are examined. Four structural types have been characterised crystallographically, including one in which both phosphine ligands were substituted at the unique ruthenium vertex. In solution, there are many more isomers present, most of which are rapidly interconverting via hydride migrations. Substitution appears to be directed electronically to the ruthenium vertex, although steric hindrance appears to drive subsequent isomerisation via migration of the second group 15 ligand.

Keywords: Heterometallic complexes; Ruthenium; Osmium; Phosphanes; Chemical exchange

1. Introduction

Heteronuclear clusters containing group homologues are of interest for the investigation of metallo-site selectivity. Among the tetranuclear clusters of the formulae $M'M_3(\mu\text{-}H)_2(CO)_{13}$, where M and M′ are the group 8 elements, three members of this family are known, viz., $FeRu_3(\mu\text{-}H)_2(CO)_{13}$, $FeOs_3(\mu\text{-}H)_2(CO)_{13}$ and $RuOs_3(\mu\text{-}H)_2(CO)_{13}$ (**1**). The phosphine substitution chemistry of $FeRu_3(\mu\text{-}H)_2(CO)_{13}$ has been investigated in quite great detail by Geoffroy and coworkers [1]. We have recently embarked on an investigation into the chemistry of **1**, especially in comparison to that established for $FeOs_3(\mu\text{-}H)_2(CO)_{13}$, as the chemistry of ruthenium and osmium are much more alike than they are to that of iron. Our investigations on the group 15 ligand monosubstituted derivatives $RuOs_3(\mu\text{-}H)_2(CO)_{12}(L)$ (where L = tertiary group 15 ligand) have been reported [2]. Herein we would like to report on the disubstituted derivatives $RuOs_3(\mu\text{-}H)_2(CO)_{11}(L)_2$.

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2. Experimental

2.1. General procedures

All reactions and manipulations were carried out under nitrogen by using standard Schlenk techniques. Solvents were purified, dried, distilled and stored under nitrogen prior to use. Routine NMR spectra and inverse-gated decoupled ^{31}P NMR spectra were acquired on a Bruker ACF300 NMR spectrometer. 2D and VT NMR spectra were acquired on a Bruker Avance DRX500 or Bruker AMX500 machine. EXSY spectra were recorded with a mixing time of 0.5 s unless otherwise stated. The solvent used was deuterated chloroform unless otherwise stated. Chemical shifts reported are referenced to that for the residual proton of the solvent for ^1H, and to 85% aqueous H_3PO_4 (external standard) for ^{31}P. Mass spectra were obtained on a Finnigan MAT95XL-T spectrometer in an *m*-nitrobenzyl alcohol matrix. Microanalyses were carried out by the microanalytical laboratory at the National University of Singapore. With the exception of **3h**, given below, the preparation of all the other cluster compounds has been described in our earlier report [2].

Table 1
Crystal data for Os,Os-**3a**, Ru,Os-**3a**, **3b**, **3c**, **3f**, Ru,Os-**3h** and Ru,Ru-**3h**

Compound	Os,Os-**3a**	Ru,Os-**3a**	**3b**	**3c**	**3f**	Ru,Os-**3h**	Ru,Ru-**3h**
Empirical formula	$C_{47}H_{32}O_{11}Os_3P_2Ru$	$C_{47}H_{32}O_{11}Os_3P_2Ru \cdot CH_2Cl_2$	$C_{47}H_{32}As_2O_{11}Os_3Ru$	$C_{47}H_{32}O_{11}Os_3RuSb_2 \cdot 1/4C_6H_{14}$	$C_{47}H_{56}O_{11}Os_3P_2Ru \cdot C_6H_{14}$	$C_{17}H_{20}O_{11}Os_3P_2Ru$	$C_{17}H_{20}O_{11}Os_3P_2Ru$
Formula weight	1506.34	1591.26	1594.24	1709.44	1616.70	1133.94	1133.94
Temperature (K)	295(2)	223(2)	293(2)	293(2)	293(2)	223(2)	223(2)
Crystal system	triclinic	triclinic	triclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/m$	$P2_1/n$	$P2_1/n$
a (Å)	11.6739(1)	12.8424(9)	11.9089(1)	9.5595(2)	10.0594(4)	9.3405(2)	11.3605(2)
b (Å)	13.0787(2)	13.7712(10)	13.6400(1)	13.9882(2)	20.3820(7)	16.8965(5)	17.256
c (Å)	17.7705(1)	17.4424(12)	14.9247(2)	20.4536(3)	14.6764(5)	17.6967(5)	14.0633(2)
α (°)	73.390(1)	73.519(2)	96.581(1)	82.950(1)	90	90	90
β (°)	71.690(1)	70.141(2)	103.390(1)	78.418(1)	106.334(1)	99.821(1)	105.159(1)
γ (°)	66.283(1)	65.718(2)	94.928(1)	74.074(1)	90	90	90
Volume (Å^3)	2318.28(4)	2607.1(3)	2326.93(4)	2569.89(8)	2887.66(18)	2751.99(13)	2660.95(6)
Z	2	2	2	2	2	4	4
ρ_c (g cm^{-3})	2.158	2.027	2.275	2.209	1.859	2.737	2.831
μ(Mo Kα) (mm^{-1})	8.642	7.790	9.953	8.764	6.945	14.510	15.006
F(000)	1408	1492	1480	1577	1556	2048	2048
Crystal size (mm^3)	$0.10 \times 0.05 \times 0.04$	$0.16 \times 0.12 \times 0.10$	$0.40 \times 0.40 \times 0.28$	$0.113 \times 0.113 \times 0.092$	$0.22 \times 0.18 \times 0.06$	$0.24 \times 0.22 \times 0.11$	$0.26 \times 0.24 \times 0.12$
θ Range (°)	2.03–29.33	2.23–26.37	2.19–29.33	1.52–29.41	2.00–29.32	2.32–29.37	2.06–29.32
Reflections collected	19382	36070	18810	19370	18971	17672	17682
Independent reflections [R_{int}]	11085 [0.0621]	10645 [0.0470]	11014 [0.0223]	12167 [0.0321]	7327 [0.0380]	6850 [0.0400]	6650 [0.0377]
Maximum and minimum transmission	0.724 and 0.479	0.510 and 0.369	0.154 and 0.074	0.527 and 0.421	0.604 and 0.357	0.264 and 0.144	0.264 and 0.131
Data/restraints/parameters	11085/4/584	10645/34/649	11014/4/584	12167/55/458	7327/183/302	6850/0/316	6650/6/313
Goodness-of-fit on F^2	1.032	1.122	1.224	1.040	1.111	1.088	1.102
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0686$ $wR_2 = 0.1133$	$R_1 = 0.0480$ $wR_2 = 0.1179$	$R_1 = 0.0368$ $wR_2 = 0.0900$	$R_1 = 0.0480$ $wR_2 = 0.1003$	$R1 = 0.0485$ $wR_2 = 0.1111$	$R_1 = 0.0346$ $wR_2 = 0.0778$	$R_1 = 0.0335$ $wR_2 = 0.0771$
R indices (all data)	$R_1 = 0.1507$ $wR_2 = 0.1450$	$R_1 = 0.0593$ $wR_2 = 0.1237$	$R_1 = 0.0445$ $wR_2 = 0.0958$	$R_1 = 0.0884$ $wR_2 = 0.1194$	$R_1 = 0.0762$ $wR_2 = 0.1257$	$R_1 = 0.0470$ $wR_2 = 0.0834$	$R_1 = 0.0420$ $wR_2 = 0.0806$
Largest differential peak and hole (e Å^{-3})	1.701 and −2.150	2.055 and −1.304	2.477 and −1.555	1.609 and −1.755	1.339 and −1.651	1.329 and −2.445	1.978 and −2.142