Journal of Organometallic Chemistry, 247 (1983) C42—C44
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

SYNTHESES OF GOLDTRIOSMIUM-ISOCYANATE CLUSTERS

KEVIN BURGESS, BRIAN F.G. JOHNSON, and JACK LEWIS*
University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW (Great Britain)

(Received November 24th, 1982)

Summary

The complexes $[Os_3(CO)_{10}(AuPEt_3)(NCO)]$ (1) and $[Os_3(CO)_{11}(AuPEt_3)(NCO)]$ (2) have been synthesised from $[Os_3(CO)_{12}]$, azide anions, and $[AuClPEt_3]$ and from the reactions of $[Os_3(CO)_{12-n}(NCMe)_n]$ (n = 1 or 2) with $[OCNAuPEt_3]$; the ^{13}C NMR spectra of the products are discussed.

Activation of $[Os_3(CO)_{12}]$ is central to the development of triosmium cluster chemistry [1]. Typically, the reactivity of a triosmium system is enhanced by introducing a reactive [2] or labile [3] ligand. Another means of activation is via heteronuclear metal—metal bonds and, because of this, there has been increasing interest in goldtriosmium clusters [4—7]. This communication describes high yielding syntheses of goldtriosmium isocyanate clusters from $[Os_3(CO)_{12}]$. These mixed-metal isocyanates are activated as a result of their heteronuclear metal—metal bonds and functionalized by isocyanate ligands.

Equimolar quantities of sodium azide, 18-crown-6, chlorogold(I)triethylphosphine, $[ClAuPEt_3]$, and $[Os_3(CO)_{12}]$ react to produce a red complex $[Os_3(CO)_{10}(AuPEt_3)(NCO)]$ (1) and a yellow complex $[Os_3(CO)_{11}(AuPEt_3)(NCO)]$ (2). Anionic metal carbonyl isocyanates have been synthesised by reactions of azide anions with monomeric metal carbonyls [8,9]. Presumably in the cluster reaction a triosmium isocyanate anion is formed as an intermediate and this reacts with the gold chloride in situ.

The products 1 and 2 were characterized on the basis of ^1H NMR, IR, and mass spectral data (Table 1), analytical data*, and unrelated syntheses. Thus, reaction of $[Os_3(CO)_{11}(NCMe)]$ with $[OCNAuPEt_3]$ affords both the decacarbonyl 1 and the undecacarbonyl 2 (eq. 1) but the $[Os_3(CO)_{10}]$-synthon $[Os_3(CO)_{10}(NCMe)_2]$ gave only the decacarbonyl $[Os_3(CO)_{10}(AuPEt_3)(NCO)]$ (1) (eq. 2) Furthermore, 1 is formed by decarbonylation of 2 in refluxing THF (eq. 3).

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*Satisfactory C, H, and N analyses were obtained for compounds 1 and 2.

TABLE 1

SPECTRAL DATA FOR $[Os_3(CO)_{10}(AuPEt_3)(NCO)]$ (1) AND $[Os_3(CO)_{11}(AuPEt_3)(NCO)]$ (2)

Compound	*m/e*	^1H NMR (ppm) in $CDCl_3$	IR (cm^{-1} in hexane)	
	^{192}Os ^{197}Au	$\delta(PCH_2CH_3)$ (m)	$\nu(NCO)$	$\nu(CO)$
1	1213 (M^+)	2.15—1.73	2300st	2093md, 2046st, 2041sh. 2012sh, 2008st, 1989w, 1981md, 1967md
2	1213 ($M^+ - 28$)[a]	2.53—1.92 (6H) 1.56—0.96 (9H)	2250br /md	2107md, 2077md, 2070md, 2052st, 2037st, 2030st, 2017md, 2007md, 1975md, 1963w, 1943w

[a] M^+ not observed.

$$Os_3(CO)_{11}(NCMe) + OCNAuPEt_3 \xrightarrow{C_6H_6,\ 1\ h,\ 20^\circ C} \underset{(1,\ 26\%)}{Os_3(CO)_{10}(AuPEt_3)(NCO)} + \underset{(2,\ 31\%)}{Os_3(CO)_{11}(AuPEt_3)(NCO)} \quad (1)$$

$$Os_3(CO)_{10}(NCMe)_2 + OCNAuPEt_3 \xrightarrow{C_6H_6,\ 16\ h,\ 20^\circ C} \underset{(1,\ 75\%)}{Os_3(CO)_{10}(AuPEt_3)(NCO)} \quad (2)$$

$$\underset{(2)}{Os_3(CO)_{11}(AuPEt_3)(NCO)} \xrightarrow{THF,\ 1\ h,\ 65^\circ C} \underset{(1,\ 80\%)}{Os_3(CO)_{10}(AuPEt_3)(NCO)} \quad (3)$$

SCHEME 1. Synthesis of $[Os_3(CO)_{10}(AuPEt_3)(NCO)]$ (1) and $[Os_3(CO)_{11}(AuPEt_3)(NCO)]$ (2).

Carbonyl-^{13}C NMR spectra of enriched samples of the isocyanates 1 and 2 are shown in Fig. 1. A 1/1/2/2/2/2 carbonyl-^{13}C NMR pattern is expected for a molecule of the type $[Os_3(CO)_{10}(\mu\text{-}X)(\mu\text{-}Y)]$ having C_{2v} symmetry. A 1/1/2/2/2/1/1 is observed for cluster 1; the signal at highest field is split presumably as a result of some slight asymmetry in the molecule. The undecacarbonyl affords 22 carbonyl resonances (counting the four most intense peaks as degenerate) and two $N^{13}CO$ signals. These data are consistent with two isomeric forms of 2 as a result of the isocyanate ligand occupying different axial (or equatorial) coordination sites.

The decacarbonyl 1 reacts with one equivalent of triphenylphosphine to form $[Os_3(CO)_9(PPh_3)(AuPEt_3)(NCO)]$, with excess triethylphosphine to give $[Os_3(CO)_9(PEt_3)_3]$, and with molecules XH (X = $PhCH_2NH$, $PhCH_2CH(CO_2Me)$-NH, HO, and MeO) to give $[Os_3(CO)_{10}(AuPEt_3)(\mu\text{-}NHCOX)]$. Full details of these reactions will be published elsewhere [10]. Similar additions to the isocyanate ligand of $[Os_3(\mu\text{-}H)(CO)_{10}(NCO)]$ have been reported [11].

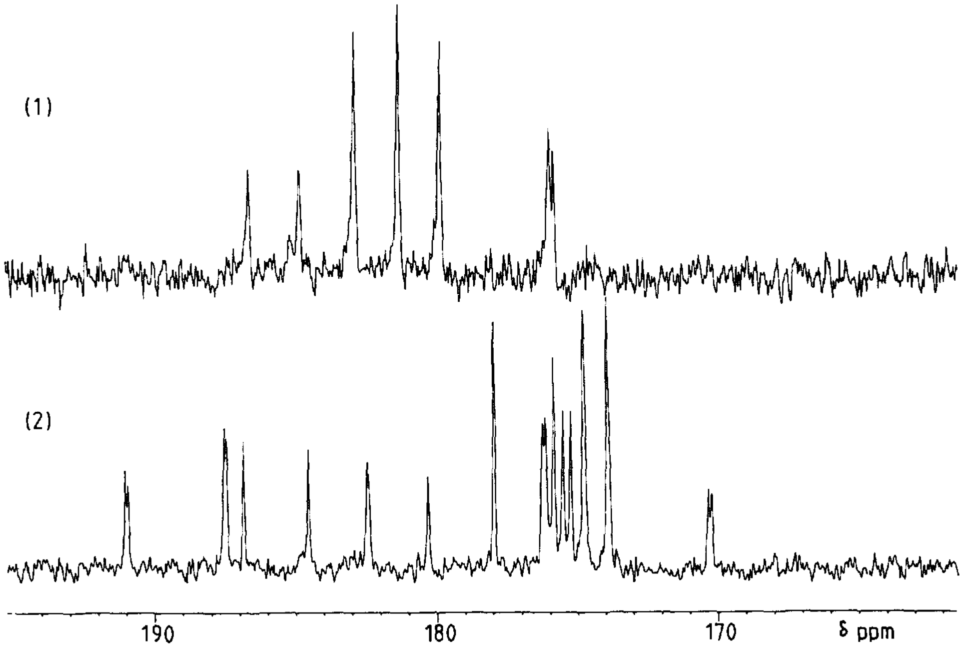

Fig. 1. ^{13}C NMR of compounds 1 and 2 in CD_2Cl_2 solution at −80°C and 250 MHz showing just the carbonyl region, δ (ppm) throughout. [$Os_3(CO)_{10}(AuPEt_3)(NCO)$] (1) assigned as a 1/1/2/2/2/1/1 pattern other signals are 134.7 (s, NCO) 19.7 (d, *J* 27 Hz, PCH_2) and 8.9 (s, CH_2CH_3); [$Os_3(CO)_{11}(AuPEt_3)(NCO)$] (2) assigned as a 1/1/1/1/1/1/1/1/2/1/1/2/1/1/2/2/1/1 pattern, other signals are 129.3 (s. NCO) 125.5 (s, NCO) 18.6 (d, *J* 28 Hz, PCH_2) and 9.2 (s, CH_2CH_3).

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