Journal of Organometallic Chemistry, 202 (1980) C39—C42
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

RELATED TRIPLY-BRIDGING LIGANDS DERIVED FROM TRIOSMIUM DODECACARBONYL AND FORMAMIDINES OR 2-AMINOPYRIDINES

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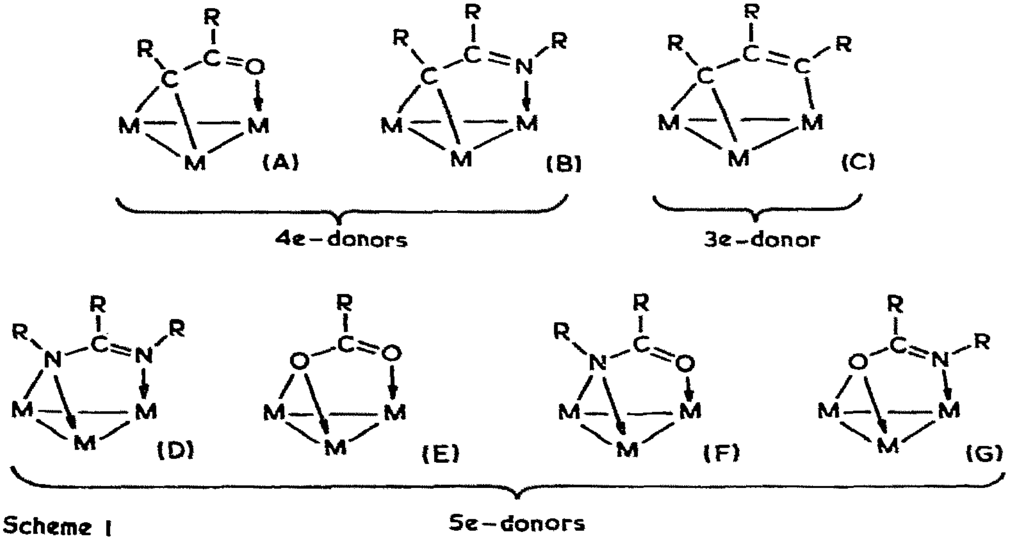
(Received September 8th, 1980)

Summary

N,N'-Dibenzyl- or diisopropyl-formamidines react with $Os_3(CO)_{12}$ or $Os_3(CO)_{10}(cyclooctene)_2$ to give different types of nonacarbonyl, $HOs_3(CO)_9$(i-PrNCHN-i-Pr) and $H_2Os_3(CO)_9(PhCH_2NCHNCH_2C_6H_4)$, the difference being in the ability of the benzyl group to be *ortho*-metallated. *N*-Benzyl-2-aminopyridine, on the other hand, gives isomers analogous to each of these clusters.

We have synthesised triosmium clusters containing μ_3-ligands of type A in Scheme 1 from aldehydes, ketones, ketene [1] and phenol and the X-ray



Scheme I

TABLE 1

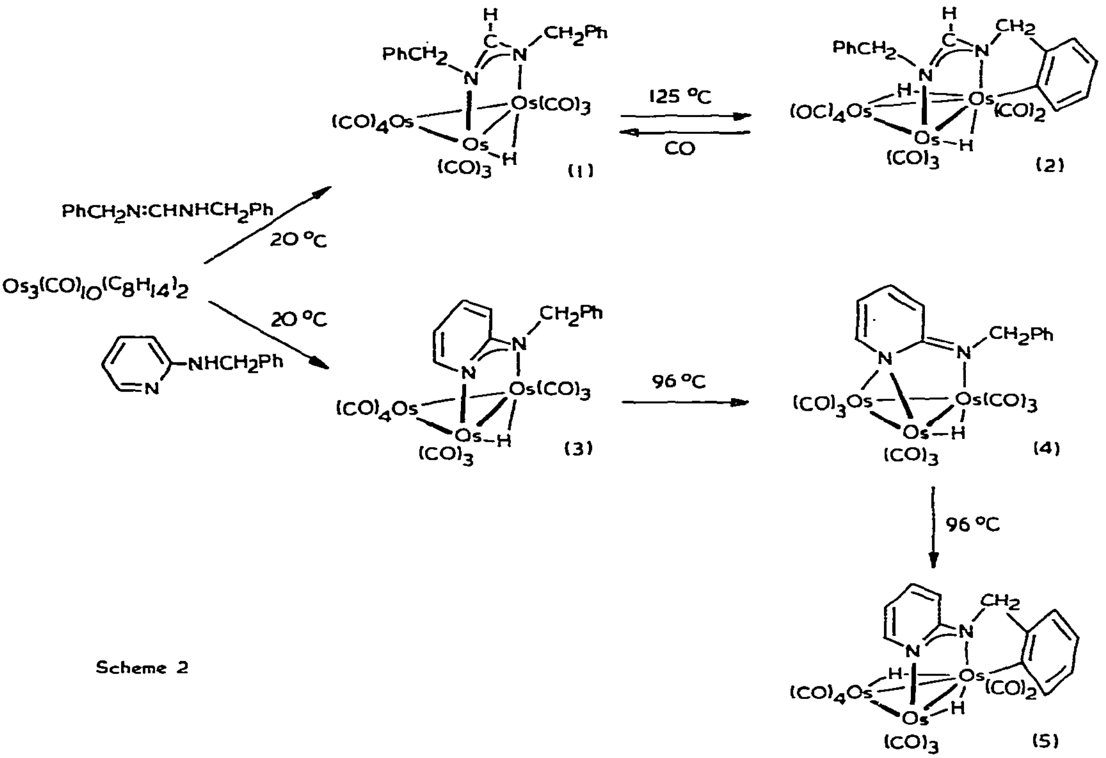
SELECTED INFRARED AND ^{1}H NMR DATA FOR THE NEW CLUSTERS[a]

Compound	ν(CO)[b] (cm^{-1})	^{1}H NMR (δ, ppm; J, Hz)[c]
$HOs_3(CO)_{10}(PhCH_2NCHNCH_2Ph)$ (1)	2106m, 2065s, 2055s, 2022s, 2004s, 1995m, 1986mw, 1975mw	7.87d, J 2 (CH); 7.29—7.14m (C_6H_5); 3.66d, 3.26d, J 14 (CH_2); −12.91d, J 2 (OsH)
$H_2Os_3(CO)_9(PhCH_2NCHNCH_2C_6H_4)$[d] (2)	2092m, 2058s, 2028s, 2010s, 2004m, 1985m, 1964m	9.48s (CH); 7.76—7.00 (C_6H_5 + C_6H_5); 4.79d, 4.33d, J 14 (CH_2); 4.69d, 4.21d, J 14 (CH_2); −11.83s, −12.17s (OsH)
$HOs_3(CO)_{10}(NC_5H_4NCH_2Ph)$ (3)	2107m, 2064s, 2057s, 2022s, 2012s, 2004m, 1995m, 1986m, 1975w	8.18dd, 6.89dt, 6.24dd, 5.95dt (NC_5H_4); 7.0—7.4 (C_6H_5); 5.02d, 4.54d, J 17 (CH_2); −11.72s (OsH)
$HOs_3(CO)_9(NC_5H_4NCH_2Ph)$ (4)	2085m, 2056s, 2029s, 2000s, 1990w, 1984m, 1977m, 1965m, 1953m	8.66d, 7.34dt, 6.64dt, 6.23dd (NC_5H_4); 7.3, 6.8—6.9 (C_6H_5); 5.40d, 4.42d, J 18 (CH_2)[e] −11.22s (OsH)
$H_2Os_3(CO)_9(NC_5H_4NCH_2C_6H_4)$[f] (5)	2091m, 2058s, 2028s, 2009s, 2005m, 1988m, 1984m, 1964s, 1933w	8.92dd, 7.5—6.0 (NC_5H_4 + C_6H_4); 4.82d, 4.40d, J 14 (CH_2); −11.08s, −12.31s (OsH)
$HOs_3(CO)_9$(i-PrNCHNPr-i)	2084m, 2054s, 2027s, 1999s, 1989vw, 1980s, 1965m, 1950m, 1937vw	9.03s (CH); 3.48sept, 2.37sept (CHMe$_2$); 1.10d, 1.03d (CH_3); −11.46s (OsH)

[a] All gave good C,H,N analyses. [b] In cyclohexane. [c] In $CDCl_3$ at 29°C at 100 MHz. [d] NMR in CD_2Cl_2. [e] AB-quartet below −30°C only. [f] NMR in CD_3COCD_3.

structure of $H_2Os_3(CO)_9(PhCH_2C_6H_3O)$ from 2-benzylphenol contains an arrangement of atoms as in **A** [2]. The recently described cluster $H_2Os_3(CO)_9$-(i-PrCCMe=NPh) adopts the corresponding structure **B** [3]. Based on **A** and **B** one can easily imagine the 3*e*- and 5*e*-donating ligands depicted in **C** to **G**. **C** is simply the σ-allyl (3*e*-donating) form of the pseudo-π-allyl (5*e*-donating) ligands well-known for ruthenium and osmium. To our knowledge no system of type **C** has been synthesised. Forms **D** to **G** are variations on μ_3-carboxylates. Our attempts to thermally decarbonylate $HOs_3(CO)_{10}(\mu_2\text{-}PhCO_2)$ have lead to a range of low yield products, none of which seems to be $HOs_3(CO)_9$-(μ_3-$PhCO_2$) [4]. We have, however, synthesised ligand systems of type **D** and **F** or **G**.

Attempting to prepare clusters of type **D**, $PhCH_2N{=}CHNHCH_2Ph$ was treated at room temperature with the bis-cyclooctene cluster $Os_3(CO)_{10}$-$(C_8H_{14})_2$ [5] in a mixture of C_8H_{14} and CH_2Cl_2 to give cluster **1** (15%) (Scheme 2). We expected the thermolysis of this in refluxing octane (1 h) to give a μ_3-$PhCH_2NCHNCH_2Ph$ cluster of type **D** but obtained instead the *ortho*-metallated cluster $H_2Os_3(CO)_9(PhCH_2NCHNCH_2C_6H_4)$ (**2**) (47%). This was isolated by TLC (SiO_2) like all the new clusters described in this paper and



Scheme 2

was characterised spectroscopically (Table 1). The corresponding reaction of *N*-benzyl-2-aminopyridine with $Os_3(CO)_{10}(C_8H_{14})_2$ gave cluster **3** (33%). Thermolysis of this complex leads to a more rapid decarbonylation and in refluxing heptane after 45 min a mixture of isomeric clusters **4** (36%) and **5** (38%). Since cluster **4** converts into **5** in refluxing heptane, no doubt this is the route by which 5 was formed. Thus although we were able to obtain a cluster of type D, this readily isomerised by an *ortho*-metallation. Clusters 1 and 3 are directly comparable spectroscopically, as are 2 and 5, and must adopt the same overall structures (Scheme 2).

It seems quite likely that 2 is formed from 1 via the cluster $HOs_3(CO)_9$-(μ_3-$PhCH_2NCHNCH_2Ph$) which was not observed because of its ease of isomerisation. The reaction of $Os_3(CO)_{12}$ with i-PrN=CHNHPr-i supports this view since after 2.5 h in refluxing octane the cluster $HOs_3(CO)_9$(μ_3-i-PrNCHNPr-i) (6) was obtained. The need for the ligand to donate 5*e* to the cluster and the close similarity between 4 and 6 strongly indicates that these ligands are triply-bridging as shown. Thus the absence of a substituent on the nitrogen atoms that can easily *ortho*-metallate allows complexes of type D to be formed, and both 2-hydroxypyridine (pyridone) and 2-aminopyridine give the clusters $HOs_3(CO)(\mu_3\text{-}NC_5H_4X)$ (X = O or NH) [6] which directly relate to cluster 4 and are of types D and F or G, respectively.

$Os_3(CO)_{12}$ reacts readily in refluxing acetic acid to give $Os_2(CO)_6(\mu_2\text{-}MeCO_2)_2$ [7] and the N-compounds in this paper are similar except that more forcing conditions are required to give the dinuclear compounds $Os_2(CO)_6(\mu_2\text{-}X)_2$ (X = NC_5H_4O from pyridone, NC_5H_4NH from 2-aminopyridine, $PhCH_2NCHNCH_2Ph$ from dibenzylformamidine and i-PrNCHNPr-i from diisopropylformamidine). We believe that the tendency for acetate to bridge is low and so the trinuclear clusters more readily breakdown into dimers than those of the corresponding N-ligands. Although we have not made any clusters of types C and E almost certainly they will be available by other routes. Furthermore, clusters with the ligand CRCRCR prefer to adopt the pseudo-π-allyl form rather than structure C and so one might expect there to be a range of complexes parallel to A to G but with two extra electrons donated from the multiple bonds.

We thank Johnson—Matthey Ltd for a loan of OsO_4 and University College London for a studentship (for R.P.).

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