Journal of Organometallic Chemistry, 228 (1982) C4—C6
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

OXIDE PROMOTED ISOMERISATION OF AN ISONITRILE COMPLEX, $H_2Os_3(CO)_{10}[CN(CH_2)_3Si(OEt)_3]$

JOHN EVANS* and BENJAMIN P. GRACEY
Department of Chemistry, The University, Southampton SO9 5NH (Great Britain)

(Received December 10th, 1981)

Summary

The isomerisation of $H_2Os_3(CO)_{10}[CN(CH_2)_3Si(OEt)_3]$ to $HOs_3(CO)_{10}$-$[CN(H)(CH_2)_3Si(OEt)_3]$ is accelerated by interaction with some oxides; both complexes afford $HOs_3(CO)_{10}[CN(H)(CH_2)_3Si(OEt)_{3-x}(O{\equiv})_x]$ as oxide supported clusters.

We report a specific isomerisation of an isonitrile complex to an aminocarbyne species during the attempted anchoring of the former to several inorganic oxides.

Two criteria required for a durable oxide tethered metal carbonyl cluster catalyst are (1) that anchoring is by a bridging ligand [1] and (2) it has some incipient unsaturation [2]. $HOs_3(CO)_9(\mu_3\text{-}\eta^2\text{-}HC{=}NPh)$ (I) fulfills both [3] and is a thermolysis product of $H_2Os_3(CO)_{10}(CNPh)$ (II) via a hydrogen migration reaction to $HOs_3(CO)_{10}(\mu\text{-}\eta^2\text{-}HC{=}NPh)$ (III). Synthesis of an oxide anchored version of I was therefore attempted.

Addition of $CN(CH_2)_3Si(OEt)_3$ [4—6] occurs readily at room temperature, as observed for other isonitriles, to yield $H_2Os_3(CO)_{10}[CN(CH_2)_3Si(OEt)_3]$ (IV) (Fig. 1). In cyclohexane solution, IV exhibited a $\nu(CN)$ at 2221 cm^{-1} and carbonyl stretching vibrations at 2099m, 2068s, 2051s, 2031s, 2023m, 2015m, 2005s, 1987m(br), 1973m and 1924w(br) cm^{-1}. At 30°C in CD_2Cl_2 solution, its ^1H NMR spectrum showed the expected isonitrile resonances: δ 3.98 (2H, t, $CN{-}CH_2$), 3.82 (6H, q, $O{-}CH_2$), 1.84 (2H, m, $CNCH_2{-}CH_2$), 1.22 (9H, t, $OCH_2{-}CH_3$) and 0.75 (2H, t, $Si{-}CH_2$). Additionally there were sets of terminal and bridging hydride resonances due to a major (δ —10.14, d, J 4 Hz and —19.77, d, J 4 Hz) and minor (δ —9.90, d, J 4 Hz and —19.68, d, J 4 Hz) isomers. These are probably due to *cis* and *trans* arrangements of the isonitrile and terminal hydride ligands. The minor isomer is more prevalent for IV (1/3) than for $H_2Os_3(CO)_{10}(CNBu^t)$ (~ 1/6).

Interaction of IV with several oxides (Al_2O_3, TiO_2, SiO_2, ZnO and MgO) at

0022-328X/82/0000—0000/$02.75

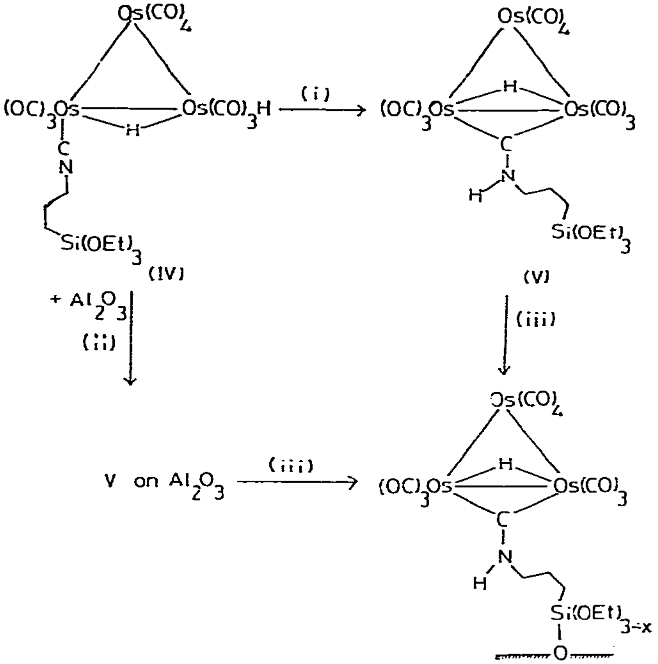

Fig. 1. (i) 35°C in CH_2Cl_2, 20 minutes, (ii) 0°C, (iii) refluxing cyclohexane, 2 h.

0°C rapidly (~2 min) gave a supported cluster which exhibited ν(CO) IR bands quite unlike those of IV (2097m, 2053vs, 2044s, 2012vs, 1999s(br), 1983s(br) and 1974s(br)) and no ν(C≡N) absorption. Complex IV itself was found to isomerise to $HOs_3(CO)_{10}[\mu\text{-}CN(H)(CH_2)_3Si(OEt)_3]$ (V) after 20 minutes in CH_2Cl_2 solution at ~35°C. (^{1}H NMR in $CDCl_3$ at 30°C: δ 9.84 (1H, br, N—*H*), 3.9 (6H, q, O—*CH*$_2$ and 2H, t, N—*CH*$_2$), 1.9 (2H, m, CH_2—*CH*$_2$—CH_2), 1.22 (9H, t, OCH_2—*CH*$_3$), 0.8 (2H, t, Si—*CH*$_2$) and −16.6 (1H, s, M—*H*) ppm). Its IR carbonyl absorptions (2098m, 2055vs, 2047s, 2015vs, 2001s, 1986s, 1978s, 1969m(sh) cm^{-1} in cyclohexane) differed only in linewidth from those observed on the oxides (Fig. 2) demonstrating that this isomerisation had also occurred during the supporting procedure. Anchored versions of V can be synthesised readily by refluxing oxide suspensions in cyclohexane solutions of IV or V for 2 h. Substitution of ethoxide groups by surface oxygens to form $HOs_3(CO)_{10}[CN(H)(CH_2)_3Si(OEt)_{3-x}(O\equiv)_x]$ was evident as ethanol elimination was detected by GLC.

CH_2Cl_2 solutions and alumina anchored versions of V were monitored for pentene isomerisation activity at 47 and 80°C. In solution (V 4.3×10^{-3} *M* and pentene 1×10^{-1} *M*), only slight activity was detected at 47°C after three days. After six days at 80°C, little *trans*-2-pentene had isomerised, but the degree of conversion of terminal to internal olefin (7 turnovers), and *cis*- to *trans*-2-pentene (12 turnovers), did increase. The alumina anchored complex exhibited similar activity at 47°C e.g. 3 turnovers for 1- going to 2-pentene, but less than 10% of the activity of V at 80°C. The IR spectra of this recovered sample indi-

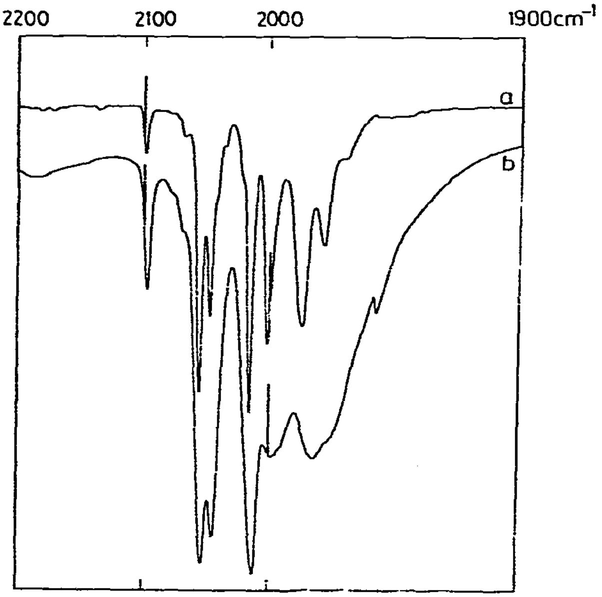

Fig. 2. IR spectra showing the carbonyl vibrations of (a) V in cyclohexane solution and (b) produced on alumina from IV (Nujol mull).

cated some complex decomposition, but it appears that the oxide environment also deactivates the intact cluster.

The presence of the silyl group in IV evidently alters the pathway of the isomerisation of the $H_2Os_3(CO)_{10}(CNR)$ derivatives [3] to cause a hydrogen transfer from osmium to the nitrogen rather than the carbon of the isonitrile ligand. Proton transfer to nitrogen was found to be catalysed by NEt_3 , probably by an ionic process [3]. Conversion of IV to V is also effected by NEt_3 , but it is also apparent that the $Si(OEt)_3$ moiety can also mediate the proton transfer, either intra- or inter-molecularly. Oxide surfaces are more efficient for the proton transfer.

It is evident that tethering complexes to oxides via isonitrile ligands can have complications due to the acidic and basic sites on the support surface.

We wish to thank the SERC for a research studentship (to BPG) and Degussa Limited for the gift of some oxides.

References

1 J. Evans and B.P. Gracey, J. Chem. Soc., Chem. Commun., (1980) 852.
2 J. Evans, Chem. Soc. Rev., 10 (1981) 159.
3 R.D. Adams and N.M. Golembeski, J. Am. Chem. Soc., 101 (1979) 2579.
4 J.A.S. Howell and M. Berry, J. Chem. Soc., Chem. Commun., (1980) 1039.
5 B.C. McKusick and M.E. Hermes, Org. Synth., 41 (1961) 14.
6 R. Appel, R. Kleinstuck and K.D. Ziehn, Angew. Chem. Int. Ed. Engl., 10 (1971) 132.