Journal of Organometallic Chemistry, 276 (1984) C65—C68
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

BRIDGING VERSUS CHELATING DIPHOSPHINE IN CLUSTERS: ISOMERS OF $Os_3(CO)_{10}$(DIPHOSPHINE)

ANTONY J. DEEMING, SUSAN DONOVAN-MTUNZI, and SHARIFF E. KABIR

Department of Chemistry, University College London, 20 Gordon Street,
London WC1H 0AJ (Great Britain)

(Received August 30th, 1984)

Summary

Isomers of $Os_3(CO)_{10}$(diphosphine) (diphosphine = $Ph_2P(CH_2)_nPPh_2$; $n = 2$ (dppe), $n = 3$ (dppp), and $n = 4$ (dppb)) have been prepared in which the diphosphine is chelating (1,1-isomer) or bridging (1,2-isomer), respectively, by displacing butadiene or acetonitrile from the complexes $Os_3(CO)_{10}$(*cis*- or *trans*-C_4H_6) or $Os_3(CO)_{10}(MeCN)_2$. $Ph_2PCH_2PPh_2$ (dppm) gives only the known bridging (1,2-isomer) whichever starting material is used. Structures have been established by infrared, ^{31}P and ^{13}C NMR methods.

Diphosphine ligands of the type $Ph_2P(CH_2)_nPPh_2$ ($n = 1$, dppm; $n = 2$, dppe; $n = 3$, dppp; $n = 4$, dppb) can chelate in mononuclear complexes but have a capacity to bridge in di- and poly-nuclear metal compounds. Dppm ($Ph_2PCH_2PPh_2$) can chelate but has been used much more as a bridging ligand [1]. The compounds $M_3(CO)_{10}$(dppm) (M = Os [2] or Ru [3]) contain bridging ligands (we will call these the 1,2-isomers). Since we have shown that $Os_3(CO)_{10}(PMe_2Ph)_2$ can be prepared as 1,1- and 1,2-isomers [4], we set out to prepare the corresponding isomers of $Os_3(CO)_{10}$(diphosphine) which would contain chelating and bridging ligands respectively.

Applying the same synthetic method as for 1,1- and 1,2-$Os_3(CO)_{10}$-$(PMe_2Ph)_2$ [4], we treated $Os_3(CO)_{10}$(*cis*-butadiene) (1,1-isomer) and $Os_3(CO)_{10}$(*trans*-butadiene) (1,2-isomer) with dppm. However, both isomers of the butadiene complex gave the same isomer of $Os_3(CO)_{10}$(dppm), the known 1,2-isomer [2], in refluxing chloroform; there was no reaction at room temperature. Table 1 gives synthetic details for compounds of type $Os_3(CO)_{10}$(diphosphine) for dppm, dppe, dppp, and dppb. For diphosphines with longer chain lengths than dppm, two isomers of the type $Os_3(CO)_{10}$(diphosphine) were obtained and identified as the 1,1-(chelating) and 1,2-(bridging)-isomers.

0022-328X/84/$03.00

TABLE 1

PRODUCTS CONTAINING DIPHOSPHINES FROM REACTION OF VARIOUS TRIOSMIUM PRECURSORS IN REFLUXING CHLOROFORM WITH AN EXCESS OF DIPHOSPHINE (1.5 mol per Os_3)

	Diphosphine	Time of reaction (h)	Diphosphine product	Yield ^{a} (%)
$Os_3(CO)_{10}$(*cis*-C_4H_6)	dppm	10	1,2-$Os_3(CO)_{10}$(dppm)	46.1
$Os_3(CO)_{10}$(*trans*-C_4H_6)	dppm	23	1,2-$Os_3(CO)_{10}$(dppm)	19.6
$Os_3(CO)_{10}$(*cis*-C_4H_6)	dppe	9	1,1-$Os_3(CO)_{10}$(dppe)	42.9
			1,2-$Os_3(CO)_{10}$(dppe)	8.6
$Os_3(CO)_{10}$(*trans*-C_4H_6)	dppe	22	1,1-$Os_3(CO)_{10}$(dppe)	8.6
			1,2-$Os_3(CO)_{10}$(dppe)	17.2
$Os_3(CO)_{10}(MeCN)_2$	dppe	3	1,2-$Os_3(CO)_{10}$(dppe)	44.6
			$Os_3(CO)_{11}$(dppe)	10.2
			1,2-$Os_3(CO)_{10}(dppe)_2$	5.3
$Os_3(CO)_{11}$(MeCN)	dppe	0.25	$Os_3(CO)_{11}$(dppe)	50.5
			$\{Os_3(CO)_{11}\}_2$(dppe)	10.2
$Os_3(CO)_{10}$(*cis*-C_4H_6)	dppp	720 ^{b}	1,1-$Os_3(CO)_{10}$(dppp)	39.1
			1,2-$Os_3(CO)_{10}$(dppp)	2.9
$Os_3(CO)_{10}$(*trans*-C_4H_6)	dppp	29	1,1-$Os_3(CO)_{10}$(dppp)	12.9
			1,2-$Os_3(CO)_{10}$(dppp)	17.1
$Os_3(CO)_{10}(MeCN)_2$	dppp	3	$Os_3(CO)_{11}$(dppp)	7.5
			1,2-$Os_3(CO)_{10}$(dppp)	20.4
			1,2-$Os_3(CO)_{10}(dppp)_2$	5.5
$Os_3(CO)_{11}$(MeCN)	dppp	0.25	$Os_3(CO)_{11}$(dppp)	44.8
			$\{Os_3(CO)_{11}\}_2$(dppp)	20.7
$Os_3(CO)_{10}$(*cis*-C_4H_6)	dppb	6	1,1-$Os_3(CO)_{10}$(dppb)	5.6
			1,2-$Os_3(CO)_{10}$(dppb)	23.6
$Os_3(CO)_{10}$(*trans*-C_4H_6)	dppb	29	1,2-$Os_3(CO)_{10}$(dppb)	25.9
$Os_3(CO)_{10}(MeCN)_2$	dppb	3.5	$Os_3(CO)_{11}$(dppb)	14.1
			1,2-$Os_3(CO)_{10}$(dppb)	18.3

^{a} Isolated yields; chromatography (TLC) on SiO_2 eluting with petroleum ether (b.p. 30—40° C)/diethyl ether mixtures. ^{b} In dichloromethane at room temperature.

(see evidence below). The reactions are not entirely selective, for example, the same two isomers are obtained by treating $Os_3(CO)_{10}$(*cis*- or *trans*-C_4H_6) with dppe but the 1,1-diene complex gives the 1,1-diphosphine compound predominantly while the 1,2-diene complex gives more 1,2-$Os_3(CO)_{10}$(dppe) than the 1,1-isomer (see Table 1). Only minor quantities of the 1,1-isomer were obtained using dppb even from the 1,1-diene compound. Other diphosphine products in Table 1 contain η^1-diphosphine or a diphosphine linking two Os_3 clusters as in the known triruthenium analogue $\{Ru_3(CO)_{11}\}_2$(μ-dppe) [5] and will be discussed in a later paper.

The structures of 1,1- and 1,2-$Os_3(CO)_{10}$(diphosphine) are based on ν(CO), and ^{13}C and ^{31}P NMR spectra. The 1,1-isomer of $Os_3(CO)_{10}$(dppe) contains a single ^{31}P NMR signal indicating equivalent ^{31}P nuclei and has a very similar ν(CO) spectrum (Fig. 1) and ^{13}C NMR spectrum to those of 1,1-$Os_3(CO)_{10}(PMe_2Ph)_2$. The $^{13}C\{^1H\}$ NMR spectrum contains signals at δ 197.9 (triplet, a), 185.8 (singlet, b), 178.2 (singlet, c), and 170.9 (singlet, d) ppm in intensity ratio 2/4/2/2 totally consistent with structure 1. The axial CO ligands (a) are coupled equivalently to the two ^{31}P nuclei (J 8.3 Hz).

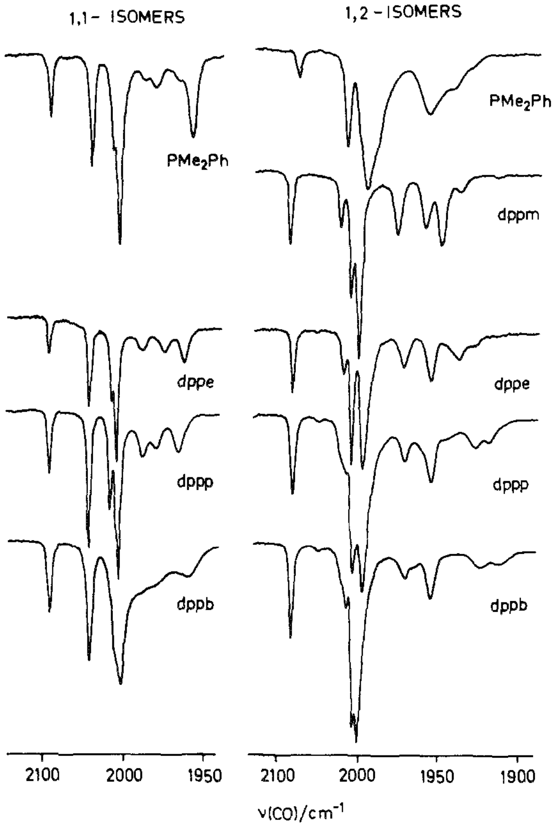
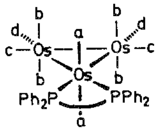


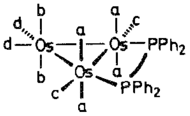
Fig. 1. Infrared spectra of 1,1- and 1,2-isomers of $Os_3(CO)_{10}$(diphosphine) and $Os_3(CO)_{10}(PMe_2Ph)_2$ recorded in cyclohexane solution except for 1,1-$Os_3(CO)_{10}$(dppb) which is in dichloromethane.

The other (1,2) isomer of $Os_3(CO)_{10}$(dppe) gives a somewhat different ν(CO) spectrum from that of 1,2-$Os_3(CO)_{10}(PMe_2Ph)_2$ because the bridging ligand necessarily occupies different sites to the PMe_2Ph ligands; the bis(phosphine) complex exists in solution as a mixture of 3 and 4, neither corresponding to structure 2. The $^{13}C\{^1H\}$ NMR spectrum of 1,2-$Os_3(CO)_{10}$(dppe) at −20°C gives singlets at δ 194.1 (a), 185.9 (b), 180.1 (c), and 174.5 (d) in the intensity ratio 4/2/2/2 consistent with structure 2. Very similar spectra were obtained for the related dppm, dppp, and dppb species except that the rates of a process leading to coalescence of the signals due to carbonyls (a) and (c) are very different. Coalescence temperatures are $\gg$50°C (dppm), >24°C (dppe), ~24°C (dppp), and <−50°C (dppb). This exchange is believed to involve a merry-go-round mechanism with a di-μ-CO intermediate with an $Fe_3(CO)_{12}$-type structure. The comptabilities of the bridged carbonyl structure with a diphosphine spanning the same two osmium atoms as the μ-CO ligands are presumably very dependent upon the diphosphine. The cluster 1,2-$Os_3(CO)_{10}$(dppb) is presumably the most geometrically flexible and has the lowest coalescence temperature.

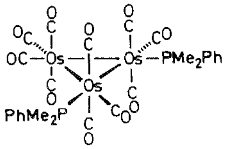
The ring conformations in these complexes are of interest because this is the first complete series of chelating and bridging diphosphine complexes with different ring sizes for direct comparison. Conformational effects are indicated by the low-temperature $^{13}C\{^1H\}$ NMR spectrum of 1,2-$Os_3(CO)_{10}$(dppe). The δ 194.1 ppm signal for the axial carbonyls (a) splits into two equal intensity signals at δ 196.5 (a′) and 192.3 (a″) at −50°C and below. There is no plane of symmetry through the three osmium atoms except by time-averaging. We cannot tell whether **5** or **6** represents the static structure. No such effects have yet been observed for the other compounds.



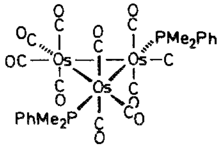
(1)



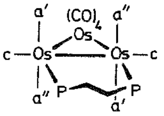
(2)



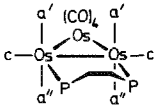
(3)



(4)



(5)



(6)

Acknowledgements. We thank the SERC for support, the Association of Commonwealth Universities for a studentship (for SEK) and Johnson—Matthey Ltd for a generous loan of osmium tetraoxide.

References

1 R.J. Puddephatt, Chem. Soc. Rev., 12 (1983) 99, and ref. therein.
2 J.A. Clucas, D.F. Foster, M.M. Harding, and A.K. Smith, J. Chem. Soc., Chem. Commun., (1984) 949 and S.R. Hodge, B.F.G. Johnson, and J. Lewis, personal communication.
3 F.A. Cotton and B.E. Hanson, Inorg. Chem., 16 (1977) 3369.
4 A.J. Deeming, S. Donovan-Mtunzi, S.E. Kabir, and P.J. Manning, J. Chem. Soc., Dalton Trans., in press.
5 M.I. Bruce, D.C. Kehoe, J.G. Matisons, B.K. Nicholson, P.H. Rieger, and M.L. Williams, J. Chem. Soc., Chem. Commun., (1982) 442.