Inorganica Chimica Acta, 111 (1986) 95–98

Solution Structures and Dynamics of [$HOs_3(CO)_{10}(\sigma,\pi$ vinyl)] Complexes

SILVIO AIME, ROBERTO GOBETTO, DOMENICO OSELLA

Istituto di Chimica Generale ed Inorganica, Facoltà di Scienze M.F.N. Università di Torino, Corso M. D'Azeglio 48, 10125 Turin, Italy

LUCIANO MILONE

Istituto di Chimica Generale ed Inorganica, Facoltà di Farmacia, Università di Torino, Via P. Giuria, 9, 10125 Turin, Italy

EDWARD ROSENBERG and ERIC V. ANSLYN

Department of Chemistry, California State University, Northridge, Calif. 91330, U.S.A.

Received March 18, 1985

Abstract

No interconversion has been found to occur on the NMR time scale between the structural arrangements found in the solid state. The σ, π motion of the vinyl group does not cause a *cis–trans* interconversion of the terminal hydrogens in [$HOs_3(CO)_{10}(CH{=}CH_2)$] which simply takes place by alternating the π-electron cloud to opposite osmium centres.

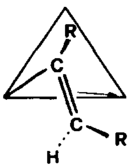
The ^1H chemical shift of the $=\mathrm{C}{<}^{\mathrm{H}}_{\mathrm{R}}$ moieties is a useful probe to assess the coordination mode of the vinyl ligand.

In [$HOs_3(CO)_{10}(CPh{=}C(H)Ph)$], a trigonal twist process has been shown to occur at the $Os(CO)_4$ unit. For the same unit $^2J_{C-C}$ *trans* have been obtained for all the reported derivatives and their magnitude is almost unchanged along the series. Further J_{CC} information has been obtained from a sample of [$HOs_3(CO)_{10}(CH{=}CH_2)$] C-13 labelled in the vinyl ligand.

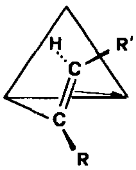
Introduction

The insertion of an alkyne molecule into the metal–hydride bond of the coordinatively unsaturated $H_2Os_3(CO)_{10}$ complex results in the formation of products of formula [$HOs_3(CO)_{10}(\sigma$, π vinyl)] in which the organic ligand acts as a three electron donor [1, 2].

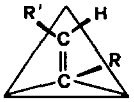
In the solid state, three different structural arrangements are found for the vinyl ligand and point out the versatility of this ligand in binding to the face of a tri-osmium cluster [structures, **I**, **II** and **III** (hydride and carbonyl groups have been omitted for clarity)] [3–8].



I



II



III

For **I** and **II** structural types in solution, it has also been shown that a σ, π rearrangement process is occurring on the NMR time scale [2]. In solution, the type **I** compound [$HOs_3(CO)_{10}(CH{=}C(H)Bu^t)$] was reported as a mixture of two isomers (*cis* + *trans*), whose occurrence was thought to arise from a decreased mobility of the σ, π bonded ligand brought about by the bulky Bu^t group [6]. These findings prompted us to examine in more detail the NMR spectra of these molecules in order to: (a) assess whether the coordination mode of the vinyl group (**I**, **II** or **III**) can be established from NMR spectra and (b) to get more insight into the intimate mechanism of the σ, π rearrangement motion and to see if any interconversion takes place among the different structural arrangements.

Results and Discussion

The ^{13}C NMR data of the complexes considered in this study are reported in Table I.

The pattern observed in the carbonyl region of the ^{13}C NMR spectra at +25 °C of all the derivatives is consistent with the occurrence of a rapid σ, π rearrangement of the vinyl ligand as already shown by Shapley *et al.* for [$HOs_3(CO)_{10}(CH{=}CH_2)$] and [$HOs_3(CO)_{10}(CPh{=}C(H)Ph)$] [9]. Careful tlc work up on the yellow mixture obtained from the reaction of $H_2Os_3(CO)_{10}$ and t-buthyl acetylene, previously reported as a mixture of type **I** isomers [6], allowed us to separate two compounds but only one of them

0020-1693/86/$3.50

© Elsevier Sequoia/Printed in Switzerland

TABLE I. ^{13}C NMR Data of $[HOs_3(CO)_{10}(\sigma, \pi \text{ vinyl})]$ Complexes[a, b, c]

Compound	COs, δ/ppm						
$[HOs_3(CO)_{10}(HC{=}CH_2)]$ [d]	185.2(1)	181.3(1)	176.3(2)	174.1(2)	173.4(2)	169.7(2)	
	at −95 °C:	184.9(1)	181.2(1)	180.1(1)	176.8(1)	174.4(1)	174.2(2)
	173.1(1)	172.6(1)	166.0(1)				
$[HOs_3(CO)_{10}(HC{=}C(H)CMe_3)]$	185.6(1)	181.8(1)	178.3(2)	176.1(2)	174.6(2)	170.7(2)	
$[HOs_3(CO)_{10}(PhC{=}C(H)Ph)]$ [e]	186.4(1)	181.4(1)	176.5(2)	175.8(2)	174.8(2)	172.4(2)	
	at −85 °C:	186.7(1)	181.8(1)	177.3(1)	176.8(1)	176.4(1)	175.9(1)
	175.7(1)	174.7(1)	173.4(1)	172.6(1)			
$[HOs_3(CO)_{10}(MeC{=}C(H)SiMe_3)]$	185.6(1)	181.9(1)	177.6(2)	177.4(2)	174.8(2)	170.8(2)	

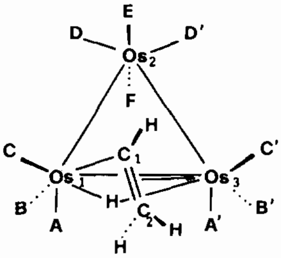
[a] CD_2Cl_2 solution. [b] Relative intensities in parenthesis. [c] Room temperature unless otherwise stated. [d] This work, ref. [9(a)]. [e] This work, ref. [9(b)].

has a composition corresponding to $[HOs_3(CO)_{10}(CH{=}C(H)Bu^t)]$. The second compound (obtained in about 40% yield) has two hydrogen less than the former and its IR, ^1H and ^{13}C NMR spectra suggest the formula $[HOs_3(CO)_{10}(C{\equiv}C\text{-}Bu^t)]$. This type of μ_2-η^2 coordination mode of an acetylide moiety has already been suggested for the analogous derivative from phenylacetylene [1]. The existence of *cis* + *trans* isomers within the framework of type **I** complexes is closely ruled out by these results.

In addition, in the case of $[HOs_3(CO)_{10}(CH{=}CH_2)]$ the ^1H NMR spectrum, in the AMX pattern, remains unchanged in the temperature range from −95 to +50 °C, confirming that the rearrangement of the vinyl ligand follows a path which does not lead to an interconversion of the geminal vinylic protons. The exchange process occurring can then be viewed as a sort of sweeping motion of the vinyl ligand on the surface of the trimetallic cluster. Further insight into the relationship between the coordination mode and the motion of the vinyl ligand has been gained by recording the C-13 NMR spectra of a sample obtained from doubly labelled C-13 acetylene. The $\{^1H\}$ C-13 NMR spectrum showed two doublets for the vinylic carbons with a carbon–carbon coupling constant $^1J_{C-C}$ of 33.4 Hz. On the basis of the established relationship between J_{C-C} and carbon–carbon distance in organic molecules [10], the small value found in this complex indicates a marked elongation of the C–C bond. However rehybridization of the carbon atoms upon coordination must be considered as well in explaining the rather small J_{C-C} coupling constant [11].

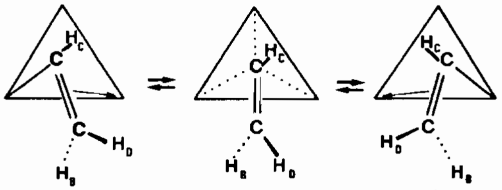
This isotopomer also allowed the detection of J_{C-C} coupling constants between the σ-bonded vinylic carbon and some of the carbonyl groups.

These coupling interactions have enabled us to make further assignments of the carbonyl resonances in these complexes. At room temperature (Fig. 1) the resonance at 178.3 ppm showed the largest J_{C-CO} (11.0 Hz) and at −100 °C this resonance is split into two signals at 180.1 and 186.8 ppm whose J_{C-CO} are 19.8 and 2.2 Hz, respectively. On the basis of the expected larger coupling between carbon in a *trans*-arrangement, these resonances can be assigned to carbonyls B and B′, respectively:



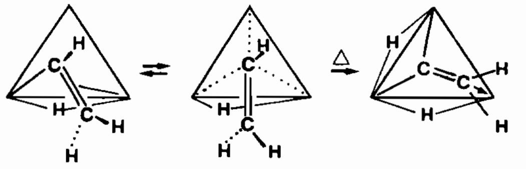
J_{C-CO} coupling on carbonyls C and C′ (which can be assigned on the basis of the coupling with the *trans*-hydride, $^2J_{H-CO} = 12.0$ Hz) results only in a slight, unresolved broadening of their resonances.

Noteworthy is the observation of the J_{C-C} coupling constants with the axial carbonyls on the unique $Os_{(2)}$ atom, 4.4 and 2.2 Hz, although a three bond transmission through the C_1–Os_1–Os_2–CO framework cannot be excluded. We think that the observed coupling constants are indicative of a direct interaction between $C_{(1)}$ and $Os_{(2)}$. The involvement of structural type **IV** as an intermediate could be responsible for this coupling pathway. This has been checked by looking at a sample highly enriched in ^{13}C. Only the $C_{(1)}$ resonance showed a marked broadening due to several unresolved overlapping couplings, whereas the $C_{(2)}$ signal was not affected. This observation supports the possible involvement of a type **IV** structure in the σ, π rearrangement of the vinyl ligand:



I **IV** **I′**

and the presence of intermediate **IV** can be invoked to explain the thermal transformation of type **I** complexes into 1:1 adducts (**V**) as reported by Deeming [12] and Shapley [2].



I **IV** **V**

An inspection of the chemical shifts found for the vinylic protons for all the reported complexes [1, 2, 8] provides the opportunity to assign the coordination mode of the σ, π vinyl group. In fact, the terminal ^1H resonance of the vinyl ligand falls in the upfield region (3.46 and 4.90 ppm) for type **I** and in the downfield region (7.12 and 8.01) for type **II** and **III** complexes, respectively. Since no drastic electronic differences are expected among the different structures (as supported from the IR spectra in the CO region) it is reasonable to assume that the difference in δ_H can be attributed to the nearest neighbour anisotropy effect of the trimetallic cluster. It then follows that the product obtained from $H_2Os_3(CO)_{10}$ and $Me-C_2-SiMe_3$ belongs to structural type **II** or **III** (*vide infra*) and on the basis of these results it seems likely that type **I** complexes are formed only from terminal alkynes, whereas the insertion of internal alkynes afford type **II** or **III** structures.

One can ascertain the occurrence of structural types **II** and **III** from the characteristic arrangement of the four CO groups on $Os_{(1)}$ in the only representative [8] of class **III** structures ($R = R' = CF_3$). Unlike types **I** and **II**, type **III** does not have a pair of *trans*-axially coordinated carbonyls on $Os_{(1)}$. A good probe to test the presence of a *trans*-relationship between a pair of coordinated carbonyls is provided by the observation of a significantly large J_{CO-CO} coupling constant. Since all the compounds reported in this study showed an almost invariant $^2J_{CO-CO}$ *trans* of 34.0 ± 0.2 Hz, it follows that $[HOs_3(CO)_{10}(MeC{=}C(H)SiMe_3)]$ belongs to type **II** structural coordination mode.

Only in the case of $[HOs_3(CO)_{10}(CH{=}CH_2)]$ and $[HOs_3(CO)_{10}(CPh{=}C(H)Ph)]$ has it been possible to observe, in the carbonyl region, spectra corresponding to 'frozen' structures, when R = H and $R' = Bu^t$, only an incipient broadening of the set of the three pairs of COs is observed at –95 °C and no broadening at all is detected at the same temperature for the derivative with R = Me and R = $SiMe_3$.

These observations suggest that the driving force for the σ, π rearrangement process is mainly related to the asymmetry induced from the substituents on the vinyl ligand rather then to the actual structural coordination mode.

Another difference among the derivatives, considered here, is represented by the behaviour of the carbonyls bound to the unique $Os_{(2)}$. No broadening of these resonances is observed for the complexes derived from HC_2H, HC_2Bu^t and $Me-C_2SiMe_3$ up to +90 °C, whereas for $[HOs_3(CO)_{10}(PhC{=}C(H)Ph)]$ a localized CO exchange is occurring.

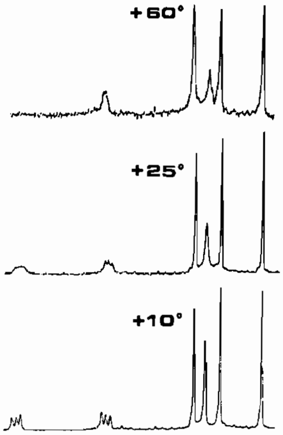


Fig. 1. V.T. C-13 NMR spectra of $[HOs_3(CO)_{10}(PhC{=}C(H)Ph)]$ (70% ^{13}CO enriched).

As shown in Fig. 1, for a highly enriched ^{13}CO sample of $[HOs_3(CO)_{10}(PhC{=}C(H)Ph)]$, as the temperature is increased two CO resonances (one axial and one equatorial of weighted intensity 2) broaden while the remaining axial one is still sharp up to +60°. At this temperature, the CO scrambling at the $Os_{(2)}(CO)_4$ unit involves all four carbonyl positions. The spectral changes observed in the temperature range +25 °C to +60 °C can be explained in terms of a selective CO exchange between one axial carbonyl group (E or F) and the two equatorial CO groups D and D′. It is our opinion that the driving force for this lower energy trigonal twist is a weak bonding interaction between Os_2 and C_1 in the transition state for $\sigma-\pi$ interchange at the organic ligand (Structure **IV**) which causes one axial carbonyl (probably E) to bend towards the equatorial carbonyls thus promoting this site exchange. A related trigonal twist rotation was already suggested by Gavens and Mays to explain the localized CO exchange process occurring at $M(CO)_4$ units in $[HM_3(CO)_{10}(\mu_2\text{-}COR)]$ derivatives (M = Fe, Os) [13]. It seems reasonable that, in this case, a weak bonding interaction between the analogous unique osmium atom $Os(CO)_4$ and a lone pair on oxygen could also cause a bending of the axial carbonyl *syn-* to the μ_2-COR ligand thus promoting a similar trigonal twist exchange. We further suggest that such a selective exchange could be general for other $H(\mu_2\text{-}L)Os_3(CO)_{10}$ systems and that the existence of a relatively strong spin–spin coupling between magnetically active nuclei in the ligand L and axial CO could be a diagnostic test for this interaction.

Experimental

$[HOs_3(CO)_{10}(HC{=}CH_2)]$, $[HOs_3(CO)_{10}(HC{=}C(H)Bu^t)]$ and $[HOs_3(CO)_{10}(PhC{=}C(H)Ph)]$ were prepared according to the published methods [1, 2, 6]. $[HOs_3(CO)_{10}(CH_3C{=}C(H)Si(CH_3)_3)]$ was synthetized similarly by reacting $H_2Os_3(CO)_{10}$ (200 mg, 0.23 mmol) and $CH_3CCSi(CH_3)_3$ (0.2 ml, 1.3 mmol) in 50 ml of n-hexane at room temperature for 12 h. Tlc work up (petroleum ether as eluant) afforded $[HOs_3(CO)_{10}(CH_3C{=}C(H)Si(CH_3)_3)]$ in ~50% yield as yellow crystals; IR (n-hexane), ν_{CO} (cm^{-1}): 2104w, 2064vs, 2051s, 2024vs, 2007s, 1996w, 1985w; ^1H NMR ($CDCl_3$), δ/ppm: 8.01(s, 1); 2.26(s, 3), 0.19(s, 9), −17.91(s, 1).

^{13}CO enrichment was performed on the parent carbonyl $Os_3(CO)_{12}$ (2 days, <1 atm of ^{13}CO in sealed vials, n-octane, 110 °C).

^{13}C-labelled acetylene (~90% enriched) was purchased from Stohler Isotope Chemicals.

The ^1H and ^{13}C NMR spectra were recorded on a Jeol GX-270/89 spectrometer.

Acknowledgements

We gratefully acknowledge the CNR (D.O.), the Italian Ministry of Education (L.M., S.A. and D.O.), the Petroleum Research Foundation (E.R., Grant No. 12685-B3) and the National Science Foundation (E.R., Grant No. CHE 8412047) for financial support. We also thank Johnson-Matthey Ltd. for a generous loan of osmium tetroxide.

References

1 A. J. Deeming, S. H. Hasso and M. Underhill, *J. Chem. Soc., Dalton Trans.*, 1614 (1975).
2 J. B. Keister and J. R. Shapley, *J. Organomet. Chem., 85,* C29 (1975).
3 A. G. Orpen, A. V. Rivers, E. G. Bryan, D. Pippard, G. M. Sheldrick and K. D. Rouse, *J. Chem. Soc., Chem. Commun.*, 723 (1978).
4 J. J. Guy, B. E. Reichert and G. M. Sheldrick, *Acta Crystallogr., Sect. B:, 32,* 3319 (1976).
5 R. G. Goudsmith, B. F. G. Johnson, J. Lewis, P. R. Raithby and W. Clegg, *Acta Crystallogr., Sect. B:, 38,* 2689 (1982).
6 E. Sappa, A. Tiripicchio and A. M. Manotti Lanfredi, *J. Organomet. Chem., 249,* 391 (1983).
7 M. Tachikawa, J. R. Shapley and C. G. Pierpont, *J. Am. Chem. Soc., 97,* 7172 (1975).
8 M. Laing, P. Sommerville, Z. Dawoodi, M. J. Mays and P. J. Wheatley, *J. Chem. Soc., Chem. Commun.*, 1035 (1978).
9 (a) J. R. Shapley, S. I. Richter, M. Tachikawa and J. B. Keister, *J. Organomet. Chem., 94,* C43 (1975); (b) A. D. Clauss, M. Tachikawa, J. R. Shapley and C. G. Pierpont, *Inorg. Chem., 20,* 1528 (1981).
10 H. Gunther and W. Herring, *Chem. Ber., 106,* 3938 (1973).
11 S. Aime, D. Osella, E. Giamello and G. Granozzi, *J. Organomet. Chem., 262,* C1 (1984).
12 A. J. Deeming, S. Hasso and M. Hunderhill, *J. Organomet. Chem., 80,* C53 (1974).
13 P. D. Gavens and M. Mays, *J. Organomet. Chem., 162,* 389 (1978).