Journal of Organometallic Chemistry, 94 (1975) C43—C46
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

FLUXIONAL BEHAVIOR OF THE BRIDGING VINYL GROUP IN $HOs_3(CO)_{10}(CHCH_2)$ AND RELATED COMPLEXES

J.R. SHAPLEY*, S.I. RICHTER, M. TACHIKAWA and J.B. KEISTER
School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801 (U.S.A.)

(Received May 27th, 1975)

Summary

^{13}C NMR spectra of the cluster complexes $HOs_3(CO)_{10}(CH{=}CHR)$ establish that the σ and π bonds binding the bridging vinylic group are rapidly interchanged between the bridged osmium atoms.

Although the scrambling processes exhibited by carbonyl ligands bound to metal cluster units are receiving considerable attention, reports of rapid intracluster rearrangements for hydrocarbon ligands are relatively rare [1-4]. We [5] (and others [6,7]) have prepared a set of osmium cluster complexes of the formula $HOs_3(CO)_{10}(CH{=}CHR)$ and proposed a structure with the vinyl group bound unsymmetrically to one edge of the metal triangle via a σ bond to one osmium atom and a π bond to the second osmium atom. We now report on ^{13}C NMR spectra of these complexes that reveal the operation of a fluxional process wherein the σ and π bonds are interchanged (see Fig. 1).

The $^{13}C-\{^1H\}$ NMR spectra (carbonyl region) obtained for $HOs_3(CO)_{10}(CH{=}CH_2)$ at various temperatures are shown in Fig. 2. Limiting spectral data are summarized in Table 1. As the temperature is raised from −67 °C

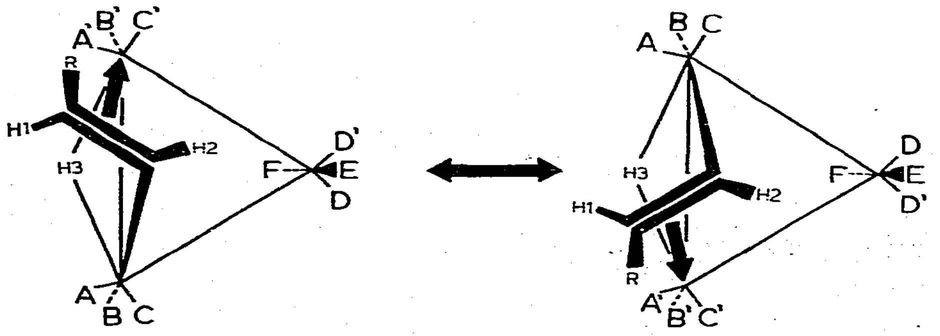

Fig. 1. Fluxional process proposed for the complexes $HOs_3(CO)_{10}(CH{=}CHR)$.

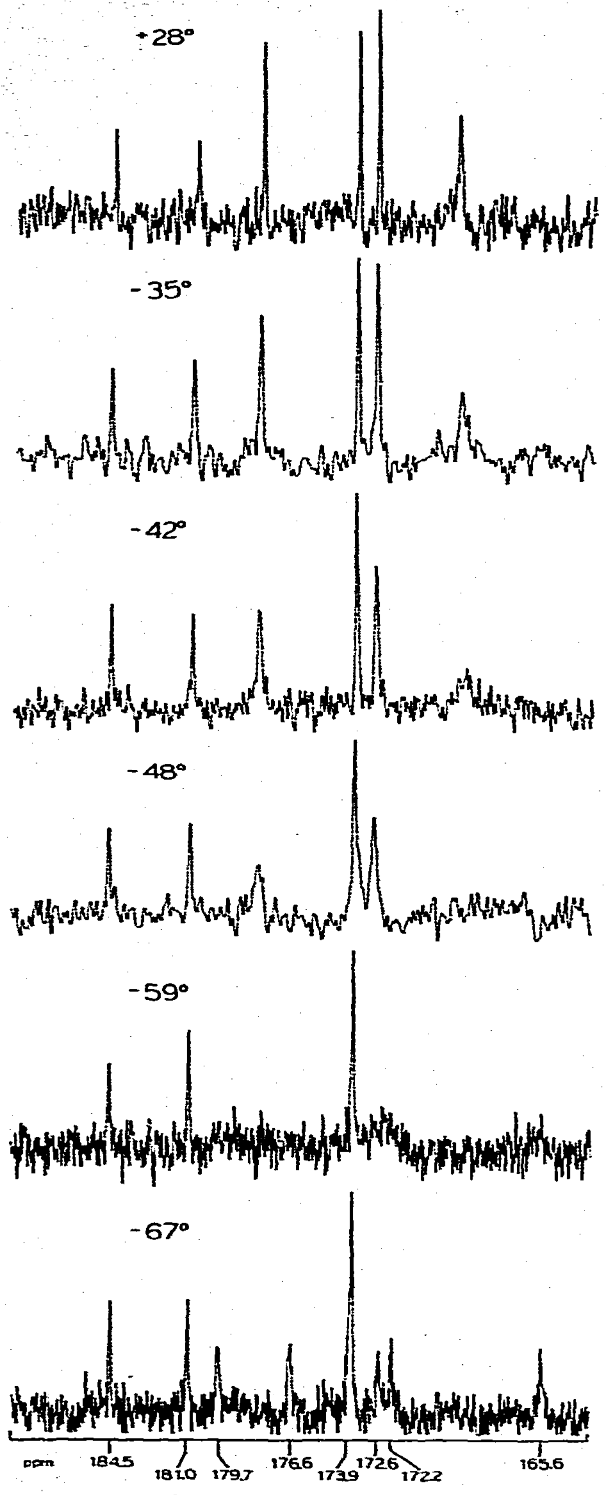

Fig. 2. ^{13}C NMR spectra (carbonyl region) for $HOs_3(CO)_{10}(CH=CH_2)$.

TABLE 1

LIMITING ^{13}C NMR DATA FOR $HOs_3(CO)_{10}(CH{=}CH_2)$ ^{a}

−67 °C			+28 °C			
peak	shift ^{b} (ppm)	rel. wt.	peak	shift ^{b} (ppm)	rel. wt.	J(C—H) (Hz) ^{c}
1	184.5	1	1	185.2	1	$\sim$0
2	181.0	1	2	181.5	1	1
3a	179.7	1				
			3	178.5	2	2.5
3b	176.6	1				
4	173.9		4	174.2	2	$\sim$0
		3				
5a	173.9					
			5	173.4	2	2
5b	172.2	1				
6a	172.6	1				
			6	169.8	2	12
6b	165.6	1				

^{a}Obtained in CD_2Cl_2 on a Varian XL-100 instrument. ^{b}Downfield from TMS, referenced to CD_2Cl_2 = 54.0. ^{c}Spectrum obtained in $CDCl_3$, proton decoupler off.

resonances arising from six individual carbons (3a, 3b; 5a, 5b; 6b; 5a overlaps 4) broaden and coalesce pair-wise to form three two-carbon singlets at 28 °C. The signals (1, 2, 4) for the the remaining four carbonyl carbons do not change significantly over this temperature range.

The spectrum observed at −67 °C for $HOs_3(CO)_{10}(CH{=}CH_2)$ is entirely consistent with the nonsymmetric structure diagrammed in Fig. 1 (R = H). The single carbon peaks (1,2), which are unchanged with temperature, are assigned to the axial carbonyls of the $Os(CO)_4$ moiety (E,F); the two-carbon portion (4) of the resonance at 173.9 ppm is assumed to be a coincidentally isochronous pair of signals from the equatorial carbonyls (D/D′). The signals that undergo coalescence are assigned to the three pairs of carbonyls flanking the edge bridged by the hydride ligand and the vinyl group (A/A′, B/B′, C/C′). Support fir this assignment comes from the hydride-carbonyl coupling constants (measured at room temperature, see Table 1), which are uniformly larger for the set of coalesced signals.

Inspection of the spectra in Fig. 2 at temperatures between −67 °C and 28 °C suggests that the pairs of signals 3a/3b, 5a/5b, and 6a/6b are averaged by the same dynamic process. In support of this point, free energies of activation derived from each pair of signals are indistinguishable ($\Delta G_c^{\ddagger}$ = 10.3 kcal mol^{-1})*. The fluxional process diagrammed in Fig. 1 is completely consistent with the spectral behavior. Interchange of the vinyl bonding mode ($\sigma \to \pi$, $\pi \to \sigma$) between the bridged metal atoms would equilibrate the carbonyl environments pairwise between the two remaining edges of the triangle (A/A′, B/B′, C/C′, D/D′) but would not equilibrate a carbonyl site above the plane of the triangle with one below (E,F). The rearrangement may be pictured as proceeding via an intermediate configuration in which the plane of the vinyl group is perpendicular to the bridged osmium—osmium bond. Conceptually, the process may be viewed

---

* $\Delta G_c^{\ddagger}$ calculated from the relations $k_c = \pi\Delta\nu/\sqrt{2}$ and $k_c = (k_b T_c/h)\exp(-\Delta G_c^{\ddagger}/RT_c)$.

as the prototype for other hydrocarbon ligand rearrangements that involve interchange of formal σ and π bonds [3, 8-10].

The complexes $HOs_3(CO)_{10}(CH{=}CHR)$ ($R = C_2H_5$, C_6H_5) each display a carbonyl ^{13}C NMR spectrum at room temperature completely analogous to that observed for $HOs_3(CO)_{10}(CH{=}CH_2)$ (Table 1). Hence, the fluxional σ,π-interchange process is inferred to be a general property of such bridging vinylic groups. Interestingly, although the prochiral groups in the complexes $HOs_3(CO)_{10}(CH{=}CHR)$ [$R = CH_2CH_3$, $CH(CH_3)_2$] would be diastereotopic in the static structure, no evidence for anisochronicity in the methylene or methyl ^1H (100 MHz) NMR signals could be established down to −90 °C. Therefore, ^{13}C NMR is uniquely suited to reveal the dynamic behavior of these compounds.

Acknowledgment

Acknowledgment is made to the Research Corporation and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. A generous loan of osmium trichloride from Engelhard Industries is also acknowledged.

References

1 F.A. Cotton, A. Davison and A. Musco, J. Amer. Chem. Soc., 89 (1967) 6796.
2 T. Yamamoto, A.R. Garber, G.M. Bodner, L.J. Todd, M.D. Rausch and S.A. Gardner, J. Organometal. Chem., 56 (1973) C23.
3 A.J. Deeming, R.E. Kimber and M. Underhill, J. Chem. Soc. Dalton, (1973) 2589.
4 S.A.R. Knox and F.G.A. Stone, Accounts Chem. Res., 7 (1974) 321.
5 J.B. Keister and J.R. Shapley, J. Organometal. Chem., 85 (1975) C29; M. Tachikawa and J.R. Shapley, unpublished work.
6 A.J. Deeming, S. Hasso and M. Underhill, J. Organometal. Chem., 80 (1974) C53.
7 W.G. Jackson, B.F.G. Johnson, J.W. Kelland, J. Lewis and K.T. Schorpp, J. Organometal. Chem., 87 (1975) C27.
8 R. Case, E.R.H. Jones, N.V. Schwartz and M.C. Whiting, Proc. Chem. Soc., (1962) 256.
9 M. Rosenblum, W.P. Giering, B. North and D. Wells, J. Organometal. Chem., 28 (1971) C17.
10 R. Aumann, Angew. Chem. Intern. Edit., 10 (1971) 560.