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Preliminary Communication

OBSERVATION OF IN-PLANE CARBONYL SCRAMBLING IN A DERIVATIVE OF DODECACARBONYLTRIOSMIUM.[1]

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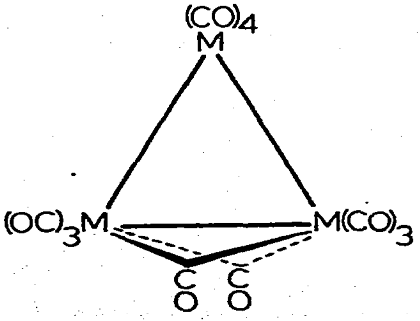
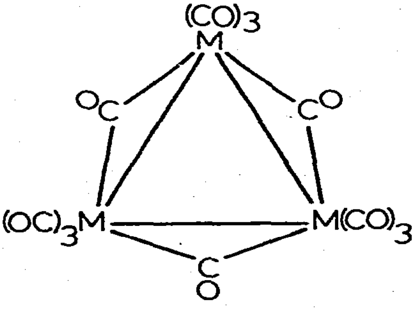
Summary

^{13}C NMR spectra obtained for the norbornadiene complex $Os_3(CO)_{10}(C_7H_8)$ indicate restricted equilibration of in-plane carbonyls via a triply bridged intermediate. Spectral assignments are facilitated by observation of significant ^{13}C-^{13}C coupling between nonequivalent trans carbonyls.

Among $M_3(CO)_{12}$ molecules (M = Fe, Ru, Os) a limiting slow-exchange ^{13}C NMR spectrum has been achieved only for $Os_3(CO)_{12}$.[2-4] Two types of carbonyl-bridged structures (I and II) have been considered as possible intermediates for carbonyl migration in unbridged $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$,[3-6] but the difficulty of dis-



I.



II

tinguishing among such scrambling processes or indeed among possible localized exchange processes (e.g., pseudo-three fold or -four fold rotations) for these highly symmetrical molecules has been discussed.[3-5] For the less symmetrical derivatives $Os_3(CO)_{12-x}(PEt_3)_x$ (x = 1,2), limiting spectra also have been obtained and the initial exchange patterns interpreted in terms of restricted scrambling via type I intermediates.[7] Examining a different kind of derivative, we have found that partially second-order ^{13}C NMR spectra of the norbornadiene complex $Os_3(CO)_{10}(C_7H_8)$[8] (1) provide evidence that the lowest energy carbonyl equilibration process traverses a configuration related to II.

The limiting low temperature ^{13}C NMR spectrum (Figure 1, -97°) of ca. 40% ^{13}CO-enriched 1 shows ten separate carbonyl resonances, consistent with an unsymmetrical, axial-equatorial substituted structure (cf. $Os_3(CO)_{10}$(s-cis-C_4H_6)[9], see Figure 2). The complex pattern of resonances at lowest field is assigned to the set of four axial carbonyls C, C', D, and D'. Each of these carbonyl carbons appears as an uncoupled singlet, if the site trans to it is occupied by a ^{12}CO (60%), and as part of an [AB] pattern (J = 35 Hz), if the trans site has a ^{13}CO (40%). Only the trans axial couplings appear to be large, as no evidence for other coupling is observed.* The unique axial carbonyl A is assigned to the next lowest field signal and the equatorial carbonyls are assigned to the higher field signals on the basis of their behavior with temperature and by comparison with the analogous signals for the 1,3-cyclohexadiene complex

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*The lack of observable axial-equatorial coupling in $Os_3(CO)_{12}$ has been mentioned previously.[3] We have observed significant coupling, indicative of axial substitution, for $Os_3(CO)_{10}(C_6H_8)$, $H_2Os_3(CO)_{10}(CNR)$, and $Os_3(CO)_{11}(CNR)$.[10]

$Os_3(CO)_{10}(C_6H_8)$.[9-11] The indication that an axial carbonyl resonates at lower field than an equatorial carbonyl on the same osmium center is consistent with assignments for related compounds.[4,7,10]

The first stage of carbonyl equilibration in 1 is observable between -90° and ca. -50°. As shown in the spectrum at -59° (Figure 1) the four complex axial carbonyl resonances become just two, two pairs of equatorial carbonyl signals are averaged, and two single carbonyl signals are unaffected. Observation of the superimposed [AB] pattern for the axial signals indicates

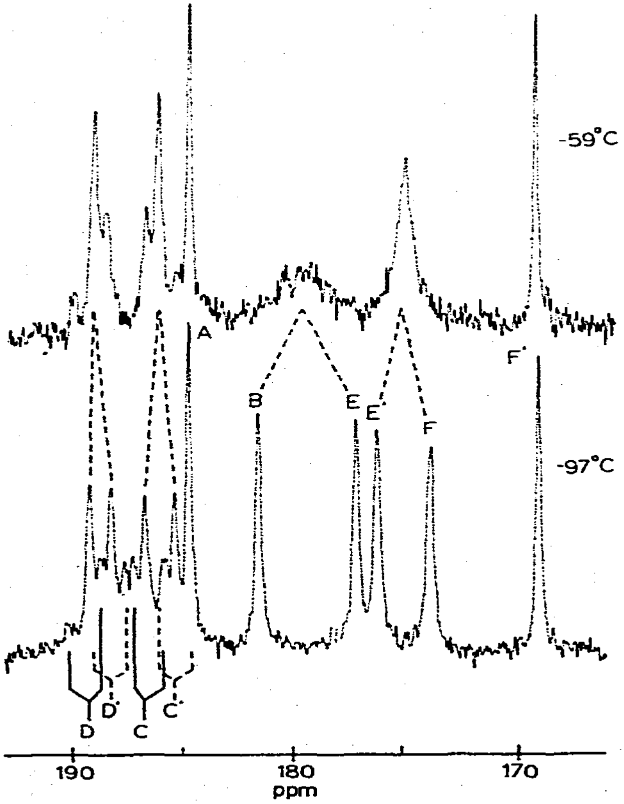

Figure 1. Limiting (-97°C) and exchange broadened (-59°C) ^{13}C NMR spectra of ^{13}CO-enriched $Os_3(CO)_{10}(C_7H_8)$. The second-order patterns due to strong ^{13}C-^{13}C coupling are indicated beneath the lower spectrum by solid and dashed lines for the pairs CD and C'D', respectively. The relative order of the coupled pairs is arbitrary.

that the trans carbonyls remain nonequivalent after the rearrangement. These features are completely reproduced in simulated spectra, which lead to an estimate of $\Delta G^{\ddagger} \sim 9.7$ kcal/mole in this temperature range.

Figure 2 shows a mechanistic interpretation of the spectral changes. Three equatorial carbonyls swing into bridging positions, then move on to new osmium atoms and reform the all-terminal structure. This process leads to pairwise equilibration among the four axial carbonyls C/C' and D/D' and among the four equatorial carbonyls B/E and E'/F. However, axial carbonyl A is not affected by this rearrangement and equatorial carbonyl F', trans through the metal-metal bond to the equatorial olefin ligand, retains that relationship even after the rearrangement.

Proton NMR spectra obtained for 1 are consistent with this mechanism. At -90° all four vinyl protons and both bridgehead protons give rise to distinct signals. As the temperature is raised to -60° the bridgehead proton signals are averaged and the four vinyl proton signals become two, indicating that the mirror plane generated by the rearrangement does not equilibrate the two double bonds. A cyclic three-fold exchange involving carbonyls A and B together with the equatorial double bond would also be consistent with these ^{1}H NMR results, but the ^{13}C NMR observation that carbonyl A remains in an axial position eliminates such a localized process.

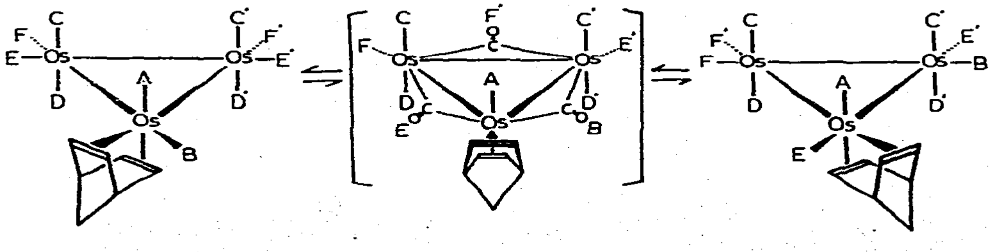

Figure 2. Mechanism suggested for the lowest energy carbonyl scrambling process in $Os_3(CO)_{10}(C_7H_8)$.

A process involving direct interchange of carbonyl B with the equatorial olefin ligand could also fit both the ^{1}H and ^{13}C NMR results. To be consistent with the spectra in Figure 1, carbonyl B would have to be assigned to the highest field signal, which remains unchanged between -97° and -59°. This assignment conflicts with data we have accumulated for several other compounds of the formula $Os_3(CO)_{10}$(diene).[10] Furthermore, this mechanism seems unlikely on physical grounds, since the intermediate configuration would have both double bonds and both carbonyls in the same plane perpendicular to the Os_3 plane.

At temperatures above -50° all of the ^{13}C NMR signals observed for 1 broaden and coalesce ultimately to one peak. Analysis and simulation of this spectral behavior is continuing, but results at this stage suggest a mixture of processes involving intermediates of type I. Thus, in this derivative the type II intermediate is lower in energy than the type I intermediate and the proposal[5] of in-plane scrambling via a type II intermediate is explicitly demonstrated. However, in view of the differing conclusions for $Os_3(CO)_{10}(C_7H_8)$ and $Os_3(CO)_{12-x}(PEt_3)_x$,[7] the situation for other derivatives remains of interest.

Acknowledgment

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