Unexpected Differences in the Rate of Ring-Whizzing in Isomeric (η^3-C_7H_7)Os(CO)$_3$(SnPh$_3$) Compounds

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Summary: In solution (η^3-C_7H_7)Os(CO)$_3$(SnPh$_3$) (**1**) exists as a mixture of distinct and noninterconverting geometrical isomers, asymmetric *mer*-**1a** and symmetric *fac*-**1b**. Ring-whizzing in **1a** is much faster than in **1b**. A higher energy process also exchanges specifically two carbonyl groups in the former.

The fluxional behavior of polyene and polyenyl transition-metal complexes and the applicability of the Woodward–Hoffmann symmetry rules to rationalize the metal shifts in these systems continue to be of general interest and a topic of some debate.[1] Mingos[2] was the first to show, on the basis of valence-bond description of the bonding, how these rules applied to π-bonded ligands. Mann[3] has further extended the treatment to show that under symmetry control, metal shifts also entail specific movements of the remaining ancillary ligands. Thus analysis of both types of rearrangement, within the same molecule, is necessary to confirm or reject the suitability of the symmetry rules. Unfortunately the number of realistic test cases remain very limited indeed. A nice example is provided by Mann[3] who showed that in the case of (η^4-C_8H_8)Fe(CO)$_2$(CN-*i*-Pr), ligand movement on iron follows the requirements set by the allowed [1,5]-suprafacial sigmatropic shift of one of the metal–cyclooctatetraene bonds (i.e., a 1,2-metal shift). Here we wish to report another compelling example which has direct, if not supportive, bearing on this point.

(η^3-C_7H_7)Os(CO)$_3$(SnPh$_3$) (**1**) is conveniently synthesized from [(η^3-C_7H_7)Os(CO)$_3$]$^-$ and Ph$_3$SnCl.[4] In accord with expectations,[1,5] the η^3-C_7H_7 ring in **1** is fluxional. Unexpectedly, the ^{1}H NMR spectrum at room temperature in toluene shows not one but *two* averaged C_7H_7 signals at δ 4.40 (sharp s) and 4.63 (br s) in a 3.4:1 ratio. At higher temperatures the broad signal at δ 4.63 sharpens noticeably, but the ratio between the two peaks remains virtually the same. Clearly, **1** exists in solution as a mixture of two fluxional but noninterconverting geometrical isomers. An unambiguous verification of this was obtained from the variable-temperature ^{13}C NMR spectra (Figure 1). At the low-temperature limit, 11 cycloheptatrienyl and five carbonyl carbon signals are observed, consistent with the presence of asymmetric meridional (**1a**) and symmetric facial (**1b**) "pseudooctahedral" molecules.[6] Exhaustive decoupling experiments revealed the unique assignment appearing in the figure.

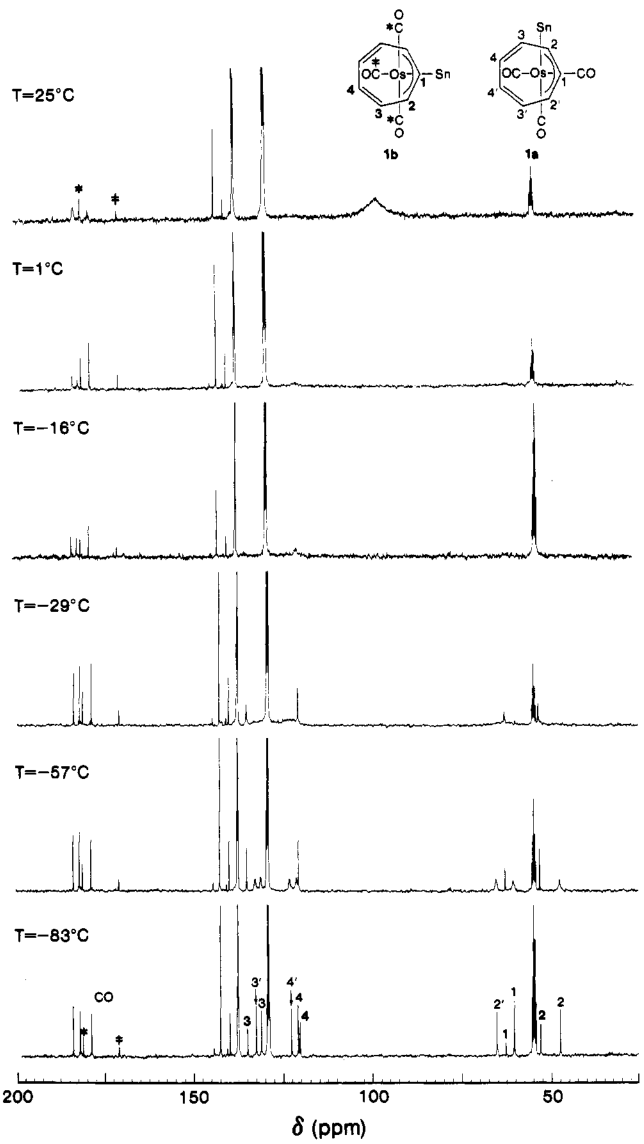
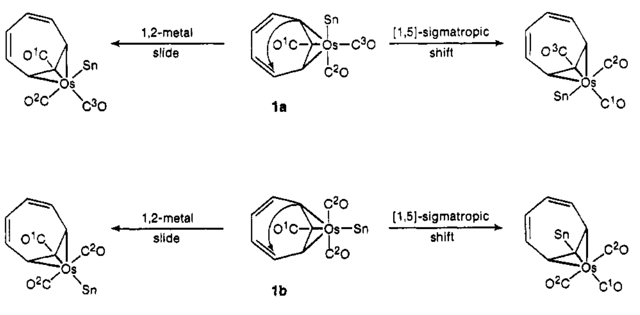


Figure 1. Variable-temperature ^{13}C NMR spectra of (η^3-C_7H_7)Os(CO)$_3$SnPh$_3$ in CD$_2$Cl$_2$.

Scheme I



As the temperature is raised, the resonances broaden but, unmistakably, the signals assigned to the asymmetric isomer **1a** coalesce much more rapidly than those of the symmetric form **1b**. This indicates a faster ring-whizzing process in the former. Specific line-shape changes are also seen in the carbonyl region. The resonances assigned to the symmetric isomer **1b** show no temperature dependence. On the other hand two, and only two, of the three carbonyl signals of the asymmetric form **1a** broaden and average to a single broad line at room temperature.

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(4) Synthetic details will appear in a forthcoming article. **1**: orange-red solid; IR (ν_{CO}, cm^{-1}, pentane) 2077 m, 2065 s, 2008 s, 1987 s; ^{1}H NMR (δ, *J*, Hz, CD$_2$Cl$_2$, −94 °C), 7.65–7.37 (m, C_6H_5), 5.98 (H*3*, br t, *J* = 9) 5.85 (H3′, dd, *J* = 8, 12), 5.44 (H2′, br t, *J* = 8), 5.26 (H3, dd, *J* = 8, 12), 5.16 (H*4*, dd, *J* = 4, 8), 5.01 (H4′, dd, *J* = 8, 12), 4.91 (H4, dd, *J* = 8, 12), 4.40 (H2 and H2, br m), 3.39 (H*1*, t, *J* = 8), 2.97 (H1, t, *J* = 5); ^{13}C NMR (δ, CD$_2$Cl$_2$, −83 °C) 183.0, 181.1, 177.8 (CO, **1a**), 180.3, 170.3 (CO, **1b**), 133.9 (C*3*), 131.4 (C3), 130.0 (C3′), 121.6 (C4′), 119.8 (C4), 119.3 (C*4*), 64.3 (C2′), 61.7 (C*1*), 59.4 (C1), 51.9 (C2), 46.3 (C2); yield 65%. Anal. $C_{28}H_{22}O_3OsSn$: C, H.

(5) Reuvers, J. G. A. Ph.D. Thesis, University of Alberta, 1979. Reuvers, J. G. A.; Takats, J., manuscript in preparation.

(6) We follow the usual convention of considering the "η^3-allyl" fragment as occupying two coordination positions in assigning six-coordinate "pseudooctahedral" geometry to compound 1.

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As shown in Scheme I, operation of the allowed [1,5]-sigmatropic shift could explain both experimental observations. Indeed this mechanism interchanges enantiomeric asymmetric forms in a single step whereas the same process in **1b** would give a higher energy alternate symmetric isomer, thus accounting for the higher energy (slower rate) for the rearrangement in **1b**. It is also clear that the allowed process would exchange the two axial carbonyl groups of the *mer* isomer **1a** in apparent harmony of the experimental results. However a closer examination of the figure reveals that, contrary to the requirements of the [1,5]-sigmatropic shifts, the two processes (ring-whizzing and CO exchange) are not coupled. For instance in the −29 °C spectrum the carbon signals of **1a** have virtually coalesced, whereas the carbonyl resonances show little broadening. Since it does not occur via symmetry-allowed [1,5]-shifts, a simple explanation for the low-temperature ring-whizzing motion in both **1a** and **1b** could be a 1,2-sliding movement of the rigid $Os(CO)_3SnPh_3$ moiety over the π-surface of the cycloheptatrienyl ring[7] (left-hand side of Scheme I). This then leaves the large difference in fluxionality between **1a** and **1b** unanswered. Also the specific exchange of only two carbonyls in **1a** at higher temperatures is surprising and implies perhaps the onset of the "allowed" [1,5]-sigmatropic shifts.

Work is underway to fully quantify the energetics of the different exchange processes and to resolve the ambiguities and questions raised by the experimental results concerning the applicability of the symmetry rules to this type of $(\eta^3\text{-}C_7H_7)ML_4$ compounds.

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[7] (a) Confirmation of the 1,2-metal shift in **1a** has been secured by both spin saturation transfer (Kiel, G.-Y., unpublished results) and selective inversion-recovery experiments (Muhandiram, D. R.; McClung, R. E. D., personal communication). (b) The slower coalescence of the carbon-4 signal in **1b** (Figure 1, $T = -29$ °C) indicates that 1,2-metal shift operates in this isomer as well. Symmetry rule on the other hand would predict an overall 1,3-metal shift since two consecutive [1,5]-sigmatropic shifts are required for return to the original molecule. Thus it appears that the high energy of the putative alternate symmetric intermediate aborts the Woodward–Hoffmann path and opens up simple 1,2-slide of the metal in **1b** also.

Uranium–Carbon Multiple-Bond Chemistry. 9.[1] The Insertion of Ph—N=C=O into the Uranium–Carbon Bond of Cp_3U=CHP(Ph)(R)(Me) To Form Cp_3U[(NPh)(O)CCHP(Ph)(R)(Me)]

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Summary: The reaction of $Cp_3U{=}CHP(CH_3)(R)(C_6H_5)$ (**1a**, R = CH_3; **1b**, R = C_6H_5) with Ph—N=C=O gives $Cp_3U[(NPh)(O)CCHP(CH_3)(C_6H_5)(R)]$ (**2a**, R = CH_3; **2b**, R = C_6H_5). The crystal structure of **2a**, space group $P2_1/c$ with $a = 13.402$ (2) Å, $b = 11.653$ (1) Å, $c = 23.209$ (3) Å, $\beta = 112.18$ (1)°, $V = 3357.3$ (8) Å^3, $Z = 4$, $R = 5.79\%$, and $R_G = 6.48\%$, has been determined. It is the first Cp_3UXY complex with a four-membered chelate ring to be structurally characterized.

Carbon dioxide inserts into both transition-metal-[2-4] and actinide–carbon[5] single bonds to form new carbon–carbon single bonds, thus producing carboxylates. The insertion of other hetereocumulenes, including isocyanates, R—N=C=O, that are analogous to CO_2 are also important.[6] In contrast to the extensive chemistry with metal–carbon single bonds, very little is knwon about the behavior of CO_2 or its analogues with metal–carbon multiple bonds. While the addition of hetereocumulenes to matel–carbon multiple bonds[7] has been reported and an insertion occurs during a rather complex reaction of CyNCO with a tungsten alkylidene,[8] no compound that results from the insertion of a single heterocumulene molecule into a structurally characterized metal–carbon multiple bond has yet been described.

We are interested in utilizing the oxygen and nitrogen affinity of actinides to activate small molecules. In this regard we have determined that the α-carbon atom in Cp_3U=CHPMePhR (Me = CH_3; Ph = C_6H_5; **1a**, R = Me; **1b**, R = Ph) is a strong nucleophile[9] and that polar-unsaturated molecules including CO,[10] RCN,[11] RNC,[12] and metal carbonyls[1,13] will insert into the uranium carbon multiple bond of **1**. A common feature in all these insertion reactions is the formation of a complex in which the heteroatom is tightly bound to uranium and which contains a carbon–carbon multiple bond formed from the four electrons of the U=C bond. The resulting metal–carbonyl insertion products will undergo further reactions which include C–O bond cleavage,[14] carbonyl coupling,[15] and metal migration.[1] On the basis of this chemistry we expected that CO_2, or CO_2 analogues such as R—N=C=O, might also insert into the uranium–carbon multiple bond of **1**. Such reactions would be particularly interesting because they would represent a new facet of f-element–CO_2 and related chemistry.

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