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Preliminary communication

REACTION OF ETHYLENE WITH THE UNSATURATED CLUSTER COMPLEX $H_2Os_3(CO)_{10}$

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Summary

Treatment of $H_2Os_3(CO)_{10}$ with excess ethylene forms ethane and a hydridovinyl cluster complex $HOs_3(CO)_{10}(CHCH_2)$, which rearranges in refluxing octane to the vinylidene complex $H_2Os_3(CO)_9(CCH_2)$.

Several recent investigations have demonstrated activation of C—H bonds by interaction with ruthenium and osmium carbonyl cluster complexes [1-3]. In order to identify and study possible intermediates in such reactions, it appeared desirable to avoid the moderately high temperatures necessary to generate reactive metal species from the saturated metal clusters commonly used (e.g., $Ru_3(CO)_{12}$ or $Os_3(CO)_{12}$. We have found that the unsaturated hydridocarbonyl cluster $H_2Os_3(CO)_{10}$ reacts with a variety of electron donor species under very mild conditions, and a recent brief report [4] of a hydridovinyl complex formed from $H_2Os_3(CO)_{10}$ and acetylene prompts us to describe our results with the same complex as prepared by a novel reaction with ethylene.

A hexane solution of $H_2Os_3(CO)_{10}$ (300 mg/50 ml) was stirred under 50 psig ethylene in a pressure bottle [5] for 40 h at 25°. Chromatography of the reaction mixture provided the major product as dark orange crystals (245 mg, 79%, m.p. 107-110° (dec.) after recrystallization from pentane). Mass spectral (*m/e* 884 (^{192}Os)) and proton NMR data (see Table 1 and Ia, Ib) confirm the composition of the compound as $HOs_3(CO)_{10}(CHCH_2)$ (I). The complex IR spectrum of I (ν(CO) at 2110w, 2066vs, 2058s, 2026vs, 2018s, 2014m (sh), 1998m, 1989 w (sh), 1984w in cyclohexane) indicates a structure with terminal carbonyls but little or no symmetry, while the chemical shifts imply that both the hydride and the vinyl group are bridging. A structure in which both ligands are placed on one edge of an osmium triangle agrees most closely with the structures of related complexes and with the eighteen-electron rule, although delocalized bonding on

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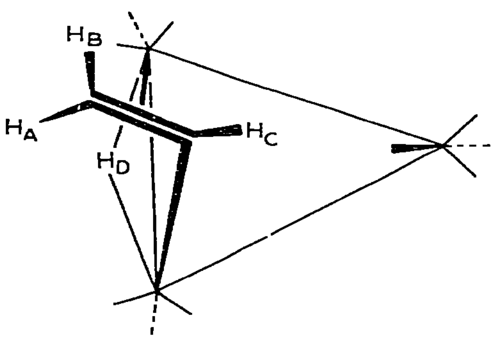
TABLE 1

PROTON NMR DATA FOR $HOs_3(CO)_{10}(CHCH_2)$ (I) [a]

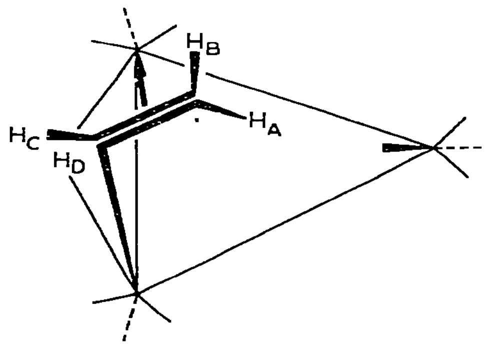
Resonance [b] τ (ppm)	Assignment [c]	Coupling constants [d] (Hz)
6.57	H_A	J_{AB} 2.8, J_{AC} 14.7, J_{BC} 9.6
5.00	H_B	
2.41	H_C	J_{AD} 0.8, J_{BD} 2.0, J_{CD} 1.6
29.36	H_D	

[a] Obtained in $CDCl_3$ at 33° on a Varian HA-100 instrument. [b] Each signal corresponds to one proton coupled (first order) to each of three other nonequivalent protons. [c] See configurations Ia, Ib. [d] Coupling constants confirmed by complete decoupling experiments.

the bridged edge is required to equalize the electron distribution between the two osmium centers. A molecular model suggests that either Ia or Ib* (shown with localized bonds) is a possible configuration.



(Ia)



(Ib)

When the reaction of ethylene with $H_2Os_3(CO)_{10}$ was carried out in a sealed NMR tube, ethane (approximately one mole per mole of I formed) was identified as a product. Furthermore, treatment of $D_2Os_3(CO)_{10}$** with C_2H_4 in the pressure bottle gave I with no D incorporated, as judged by NMR and mass spectroscopy. These results suggest that the hydrogen originally present in $H_2Os_3(CO)_{10}$ is transferred to one molecule of ethylene to form ethane and that transfer is complete before the C—H bond of a second ethylene is cleaved to form I***. Although we have not obtained direct evidence for an initial complex of $H_2Os_3(CO)_{10}$ with ethylene, it is made plausible by separate experiments in which we have isolated 1/1 complexes with such two-electron donors as CO and $P(C_6H_5)_3$ [7].

A solution of I in octane (93 mg/60 ml) refluxed under nitrogen for 36 h gave $Os_3(CO)_{12}$ (21 mg) and the previously reported [4] complex $H_2Os_3(CO)_9(CCH_2)$ (II) (30 mg after chromatography). This rearrangement of I to II strongly suggests that I is an intermediate in the formation of II directly from $Os_3(CO)_{12}$

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*An attempt to distinguish between Ia and Ib by using the nuclear Overhauser effect (H_A or H_C closer to H_D) was not successful.

**Prepared from D_2 and $Os_3(CO)_{12}$ in octane at 110° in the same manner as $H_2Os_3(CO)_{10}$ [6].

***A possible reactive intermediate in this sequence is $Os_3(CO)_{10}$. We are seeking further information concerning its existence.

and ethylene at 120° [4]. The infrared and NMR data we have obtained on II agree very closely with the data reported by Deeming and Underhill, except that one of the hydride signals (at τ 28.18 in $CDCl_3$) appears as a doublet of triplets (J(H—H) 1.6 Hz, J(H—CH_2) 0.7 Hz) rather than as simply a doublet. This observation provides further support for hydrogen positions as in the previously preferred structure (a vinylidene group with the hydride ligands on separate edges). Furthermore, it allows the tentative assignment of the τ 28.18 signal to the hydride positioned equivalently with respect to the two hydrogens in the vinylidene group.

We conclude that use of the unsaturated complex $H_2Os_3(CO)_{10}$ allows the isolation of a hydridovinyl reaction intermediate and that formation of the complex involves preliminary stoichiometric reduction of ethylene to ethane. Studies to further define the process of hydrogen transfer to ethylene and related species are in progress, and preliminary results indicate that the hydrogenation can be made catalytic.

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