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Preliminary Communication

TWO LIGHTLY STABILIZED DECACARBONYLTRIOSMIUM COMPLEXES[1]

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Summary

In cyclooctene solution $H_2Os_3(CO)_{10}$ reacts with ethylene to form $Os_3(CO)_{10}(C_8H_{14})_2$, which can be transformed to $Os_3(CO)_{10}(NCCH_3)_2$. These two labile complexes are useful intermediates for preparation of decacarbonyltriosmium derivatives.

Triosmium cluster derivatives have been prepared from the parent carbonyl $Os_3(CO)_{12}$[2] and from the unsaturated compound $H_2Os_3(CO)_{10}$.[3-5] The latter species has allowed observation of the initial stages of hydrocarbon activation by the triosmium unit; hydrogen transfer to an alkyne,[4a] alkene,[4b] or diene[4c] formally generates a decacarbonyltriosmium moiety that could be a reactive intermediate in the various reactions observed. Although the existence of $Os_3(CO)_{10}$ as a free species remains speculative,[3b] we have prepared "lightly stabilized" derivatives $Os_3(CO)_{10}S_2$ (S = cyclooctene, acetonitrile) that provide the decacarbonyltriosmium moiety in a general and synthetically useful fashion.

At moderate temperatures $H_2Os_3(CO)_{10}$ is indefinitely stable in cyclooctene solution. However, under an atmosphere of ethylene (15 psig) the purple solution turns yellow after ca. 12 hr. Removal of a excess cyclooctene (40°C, 0.1 mm) leaves a thermally stable yellow solid, characterized as $Os_3(CO)_{10}(C_8H_{14})_2$(1). Compound 1 decomposes rapidly when dissolved in nondonor solvents, but it is stabilized by the presence of excess cyclooctene and can be recrystallized from pentane/cyclooctene.* In benzene ^{1}H NMR signals due to the coordinated cyclooctene ligands at τ 6.55 (vinylic) and τ 7.52, 7.66 (allylic) are not obscured by free cyclooctene signals. The IR spectrum of 1 in cyclooctene shows only terminal carbonyl bands (ν_{CO}: 2097w, 2041m, 2027m, 2013s, 1990m, 1981m, 1975m, 1967, 1950 vw); its mass spectrum displays the ions $Os_3(CO)_x(C_8H_{14})^+$ (x = 1 to 10). Brief heating of 1 in toluene with excess cyclooctene forms the known dehydrocyclooctene compound $H_2Os_3(CO)_9C_8H_{12}$.[2a]

Addition of acetonitrile to a solution of 1 followed by evacuation provides $Os_3(CO)_{10}(CH_3CN)_2$ (2). Complex 2 decomposes less readily than 1; it forms moderately stable solutions in dry solvents without added acetonitrile, but it is most readily recrystallized in the presence of excess ligand.** Only terminal carbonyl bonds are observed in the IR spectrum (ν_{CO}, C_6H_{12}: 2078w, 2052w, 2022s br, 1993w sh, 1984s, 1964m); no band assignable to ν_{CN} is seen. Decomposition to $Os_3(CO)_{12}$ apparently occurs under the conditions necessary to obtain an electron-impact mass spectrum. The ^{1}H NMR spectrum of a solution of 2 with excess acetonitrile shows separate sharp signals for the bound and free ligands at 30°C. Significant line broadening without decomposition is observed in the range 50-75°C and preliminary kinetic data ($\Delta H^{\ddagger}$ = 29 kcal/mole, $\Delta S^{\ddagger}$ = +28 cal/deg mole) are consistent with a dissociative exchange process.

Benzene solutions of 1 (stabilized with cyclooctene) or 2

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*For $C_{26}H_{28}O_{10}Os_3$, calcd (found): C 29.16 (29.37), Os 53.27 (53.43).

**For $C_{14}H_6N_2O_{10}Os_3$, calcd (found): C 18.03 (18.33), H 3.00 (2.98) Os 61.17 (60.82) react readily (25°C, < 30 min) with an excess of strong donor ligand to provide $Os_3(CO)_{10}L_2$ (L = PPh_3, PPh_2Me, $PPhMe_2$, $P(OMe)_3$, CNMe, $CNCH_2Ph$) in high isolated yield. The isonitrile derivatives can also be isolated from the mixtures obtained under the conditions used previously for tertiary phosphine derivatives of $Os_3(CO)_{12}$.[6] However, proceeding from 1 or 2, it is possible to prepare mixed ligand derivatives by sequential addition of different ligands. In this manner compounds of the formula $Os_3(CO)_{10}LL'$ (e.g., L = $P(OMe)_3$, L' = $P(p\text{-tolyl})_3$) have been isolated in up to 80% yield. Several of these derivatives, including $Os_3(CO)_{10}(PMe_2Ph)_2$ and $Os_3(CO)_{10}(P(OMe)_3)_2$, at low temperatures show NMR evidence for two isomers. Clarification of the configurations adopted and study of their dynamic behavior are in progress.

Addition of an excess of various dienes to 1 or 2 produces $Os_3(CO)_{10}$(diene) complexes in good isolated yields. We have previously prepared complexes of several conjugated dienes from $H_2Os_3(CO)_{10}$,[4c] but complexes of 1,5-cyclooctadiene, norbornadiene, and 1,5-hexadiene are readily accessible only from 1 or 2.

Diphenylacetylene reacts smoothly with 1 or 2 to form $Os_3(CO)_{10}(PhC{\equiv}CPh)$.[4a] Terminal acetylenes also react readily, giving the same compounds obtained from $H_2Os_3(CO)_{10}$,[3a, 5a,7] except in higher yield due to the absence of the insertion products $HOs_3(CO)_{10}(CH{=}CHR)$.

Complexes 1 and 2 provide "$Os_3(CO)_{10}$" for reactions involving cleavage of H-Y bonds. A cyclooctene solution of 1 under hydrogen (30 psig) is quantitatively converted to $H_2Os_3(CO)_{10}$ after ca. 12 hr. Interaction of 1 or 2 with α-olefins provides the vinyl compounds $HOs_3(CO)_{10}(CH{=}CHR)$.[3a,4b,5] This is a more general route to such compounds than from $H_2Os_3(CO)_{10}$, since $H_2Os_3(CO)_{10}$ does not readily transfer hydrogen to some simple olefins (e.g., styrene).[4b] Similarly, products of the formula $HOs_3(CO)_{10}Y$, in which Y acts as a bridging three-electron donor group, have been isolated for HY = HCl, HBr, HOEt, H_2NPh, HSPh, and C_5H_5N.[8]

We have found complexes 1 and 2 to be especially useful in preparing ^{13}CO-labeled compounds in high yield.[7] However, they also provide the opportunity for systematic and quantitative study of "oxidative" addition to the triosmium unit. Further studies are in progress.

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