the butadiynediyl ligand is effective in conveying electronic information between the two metal centers in the same molecule. Work is underway to determine the extent of this interaction by studying other heterobimetallic complexes containing carbon-carbon triple bonds.

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**Supplementary Material Available:** Listings of spectroscopic data (IR, $^1H$ NMR, $^{13}C$ NMR) and analytical data for **2-6** (4 pages). Ordering information is given on any current masthead page.

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# Organometallic Synthesis via "Surface-Mediated" Reactions: High-Yield Route to $HOs_3(CO)_{10}(OH)$

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*Summary:* The silica-anchored hydrido cluster $HOs_3(CO)_{10}(OSi<)$ is easily prepared from physisorbed $Os_3(CO)_{12}$. Chemical displacement from the surface with HF leads to the isolation of pure $HOs_3(CO)_{10}(OH)$. This approach is far simpler and gives much higher yields than the conventional syntheses in solution.

The surface organometallic chemistry originating from the interaction of $Os_3(CO)_{12}$ with the surface of silica has been investigated over the last few years.[1] In particular, the oxidative addition of a silanol group of the surface into an osmium-osmium bond of the cluster takes place easily on thermal treatment in argon or under vacuum at 373 K:

$$Os_3(CO)_{12} + HO\text{-}Si< \rightarrow HOs_3(CO)_{10}(OSi<) + 2CO$$

The surface reaction is stoichiometric;[1] the surface hydride is selectively formed and is stable up to 423 K.

Solvent extraction of the surface species with $CH_2Cl_2$ or THF was unsuccessful. However, we have found that dissolution of the silica support with HF leads to destruction of the Os-O-Si bonds, and by protonation, pure $HOs_3(CO)_{10}(OH)$ is recovered:

$$HOs_3(CO)_{10}(OSi<) \xrightarrow{HF/H_2O} HOs_3(CO)_{10}(OH) + H_2SiF_6$$

The proposed chemical displacement with HF thus may provide a general method for the characterization of silica-supported metal clusters. In addition, a novel "surface-mediated" route to the high-yield synthesis of $HOs_3(CO)_{10}(OH)$ now is available.

In a typical experiment, the anchored osmium cluster $HOs_3(CO)_{10}(OSi<)$ (2.0 wt % Os) was prepared from $Os_3(CO)_{12}$ (160 mg) and $SiO_2$ (Aerosil 200 Degussa, 5.0 g) by following two different procedures: (A) $Os_3(CO)_{12}$ was first physisorbed on silica, and then the mixture was heated under argon between 373 and 413 K.[2] (B) The support was suspended in a degassed *n*-octane solution of $Os_3(CO)_{12}$ and refluxed under argon until the solvent was decolorized.[3] Once dried, $HOs_3(CO)_{10}(OSi<)$ is stable in air and can be handled without special precautions. It then was protonated at 195 K with 200 mL of degassed 20% hydrofluoric acid. In the process the solid dissolved completely. After it was warmed to room temperature, the aqueous solution was extracted three times with 100-mL portions of $CH_2Cl_2$. The yellow organic solution thus obtained was found by thin-layer chromatography to contain $HOs_3(CO)_{10}(OH)$ as the only product.

**Table I. Chemical Extraction Data from Different Samples of $HOs_3(CO)_{10}(OSi<)$**

| support[a] | technique of impregnation[b] | thermal treatment T, K | t, h | $^1H$ NMR, ppm[c] |
|---|---|---|---|---|
| Aerosil 200 | A | 420 | 12 | -12.60 |
| | B | 398 | 20 | -12.60 |
| Cab-O-Sil M5 | A | 373 | 40 | -12.65 |
| Akzo F6 | B | 398 | 6 | -12.58 |
| Carlo Erba GC | B | 398 | 6 | -12.60 |
| Porasil 80-100 | B | 398 | 14 | -12.57 |
| $HOs_3(CO)_{10}(OH)$[d] | | | | -12.58 |

[a] All supports used as received. [b] See text. [c] In $CD_2Cl_2$ at 300 K. [d] Reference 4.

The $^1H$ NMR spectrum of the solution showed a strong high-field signal at -12.60 ppm from TMS, in good agreement with the reported value for $HOs_3(CO)_{10}(OH)$.[4] In the mass spectrum, the parent ion was observed at $m/z$ = 868, with several other fragments corresponding to the successive loss of the 10 carbonyl groups. The FT-IR spectrum in *n*-pentane showed six bands in the $\nu(CO)$ region, at 2110 vw, 2069 vs, 2062 s, 2023 vs, 2000 s and 1984 m $cm^{-1}$. The yellow $CH_2Cl_2$ solution then was evaporated in vacuo. $HOs_3(CO)_{10}(OH)$ was recovered as air-stable orange crystals after recrystallization from *n*-pentane at 273 K (85.6 mg, 56% yield based on $Os_3(CO)_{12}$).

Different types of silica were used to prepare the grafted hydride. In all cases, pure $HOs_3(CO)_{10}(OH)$ was obtained after the chemical displacement with HF (see Table I). The insensitivity of the "surface-mediated" synthesis to the nature of the silica surface and/or to the preparation method is thus demonstrated.

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This new, "surface-assisted" route compares favorably with the conventional homogeneous-phase syntheses. Reduction of $Os_3(CO)_{12}$ with sodium borohydride[5] leads to the formation of complex mixtures of hydrido carbonyls; after purification by preparative TLC and recrystallization, $HOs_3(CO)_{10}(OH)$ was obtained in low yield (27%). Deeming et al.[6] reported a new synthetic route via acid-induced displacement of acetaldehyde from a ($\mu$-vinyloxy)triosmium cluster, yielding $HOs_3(CO)_{10}(OH)$ (36%) after chromatographic separation on silica. Our reported synthesis shows the effectiveness of the silica surface in providing a more efficient synthetic route to the preparation of organometallic complexes. This new field of "surface-mediated" reactions[7-9] should have promising applications in preparative organometallic chemistry.

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# A Chemical Reaction Path from Crystal Structure Data: Isolation of Intermediates in the Reaction of a Bimetallic Chiral Enolate with Benzaldehyde

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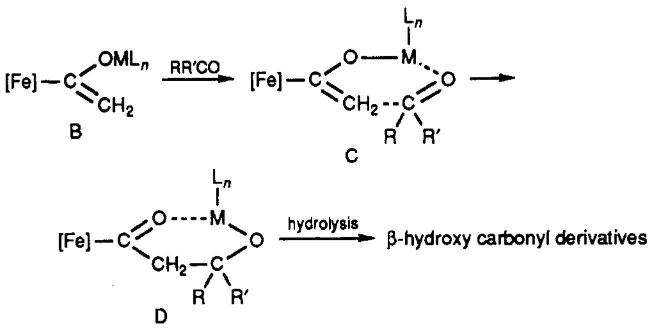
*Summary:* The isolation and the structural characterization of $[cp(CO)(PPh_3)Fe(COCH_2C(Ph)OTi(cp)_2Cl)]$ (**2**), derived from the aldol reaction of $[cp(CO)(PPh_3)Fe(C(CH_2)OTi(cp)_2Cl)]$ (**1**) with PhCHO, was achieved. When the $Cl^-$ ligand was removed from **2** with use of $BPh_4^-$, the dimetallacycle $[cp(CO)(PPh_3)Fe(COCH_2C(Ph)OTi(cp)_2)]^+$ (**3**) was obtained. Its structure very closely mimics the structure of the cyclic transition state suggested for the aldol reaction.

The chiral auxiliary $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)]$ (≡[Fe]) has been extensively developed by Liebeskind[2] and Davies[3] in the form $\{[Fe]\text{-}COCH_2^-\}$ (A) for the stereoselective delivery of the acyl fragment to organic electrophiles. Because of the important role played by the countercation $M^+$ in controlling reactivity and stereoselectivity,[2-4] our attention was focused on (i) the preparation of transition-metal derivatives of the anion A in either its keto or enolato form[5] and (ii) the elementary steps of the aldol reaction of A, in its dimetallic enolato form, first probed with PhCHO.

**Scheme I**



In a simplified scheme the aldol reaction is believed to proceed through some key steps: the cyclic transition state C and the adduct D, which has never been isolated but is hydrolyzed in the usual workup to the final $\beta$-hydroxy carbonylic derivative.[2,3,6]

In order to gain information on the intermediates sketched in Scheme I, we ran the reaction of benzaldehyde with the dimetallic version of the iron enolate A, as reported in Scheme II.

Complex 1[7] was synthesized by following the procedure

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(7) The procedure for 1 is the same as that reported for the zirconium analogue.[5] The yield is ca. 60%. The solid was recrystallized from $THF\text{-}Et_2O$ to give a red-brown crystalline solid. $\nu$(CO) (Nujol): 1918 $cm^{-1}$. $^1H$ NMR (200 MHz, $C_6D_6$): $\delta$ 3.91 (dd, 1 H, $J_{H\text{-}P} = 3.70$ Hz, $J_{gem} = 1.90$ Hz), 4.18 (pseudo t, 1 H, $J_{H\text{-}P} = 1.50$ Hz, $J_{gem} = 1.90$ Hz), 4.53 (d, 5 H, cp–Fe, $J_{cp\text{-}P} = 1.00$ Hz), 5.71 (s, 5 H), 6.20 (s, 5 H), 7.04–7.63 (m, 15 H). Anal. Calcd for $C_{36}H_{32}ClFeO_2PTi$: C, 64.84; H, 4.84; Cl, 5.32; P, 4.64. Found: C, 64.76; H, 4.82; Cl, 5.22; P, 4.54. The structure of 1 has been determined by an X-ray analysis.

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