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Hydrosilation of Alkynes by an Osmium Cluster Complex. Isolation and Structural Characterization of an Intermediate

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Summary: Reactions of the complex $Os_3(CO)_{10}(NCMe)[Si(OMe)_3](\mu\text{-}H)$ (**1a**) with the alkynes HC_2R (R = Bu^t, *p*-tolyl) yield complexes that upon treatment with CO at 68 °C produce the silylolefins *trans*-R(H)C=C(H)Si(OMe)$_3$ (R = Bu^t, *p*-tolyl). One of the complexes, $Os_3(CO)_{10}[Si(OR)_3][\mu\text{-}C(H)C(H)Bu^t]$ (**2a**; R = Me) was characterized crystallographically and found to contain a bridging η^2-*tert*-butylvinyl ligand and a terminally coordinated trimethoxysilyl group positioned cis to the bridging carbon atom of the *tert*-butylvinyl group. The characterization of this intermediate demonstrates that the mechanism of hydrosilation by this cluster complex is initiated by a hydride insertion mechanism.

The metal-catalyzed hydrosilation of olefins is a widely used process for the preparation of organosilanes.[1] The metal-catalyzed hydrosilation of alkynes is an effective method for the preparation of alkenylsilanes.[1,2] The latter reactions often lead to complex mixtures of products, and this has led to proposals of several mechanisms to account for the observed stereochemistries. Most of the mechanisms that have been proposed involve a shift of a hydride ligand from the metal to the coordinated alkyne in the first step.[3,4] However, Ojima et al. have recently shown that rhodium and mixed cobalt/rhodium carbonyl cluster complexes are effective catalysts for the hydrosilation of alkynes,[5] ketones,[6] and dienes[6] and silylformylation of alkynes,[7] and they have obtained evidence for mechanisms that involve a shift of the silyl group to the substrate in the first step. These exciting new results have prompted us to communicate some of our recent results for a related cluster system.

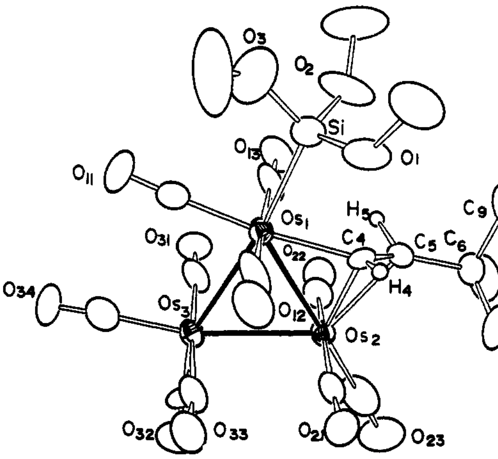

Figure 1. ORTEP diagram of $Os_3(CO)_{10}[Si(OMe)_3][\mu\text{-}C(H)=C(H)Bu^t]$ (**2a**) showing 35% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg) are as follows: Os(1)–Si = 2.427 (4), Os(1)–C(4) = 2.13 (1), Os(2)–C(4) = 2.18 (1), Os(2)–C(5) = 2.35 (1); Si–Os(1)–C(4) = 80.8 (4).

We have recently prepared and characterized the lightly stabilized cluster complexes $Os_3(CO)_{10}(NCMe)[Si(OR)_3][(\mu\text{-}H)$ (**1a**, R = Me; **1b**, R = Et).[8,9] We have now found

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[1] Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407.

[2] Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, England, 1989; Chapter 25, pp 1479–1526.

[3] Dickers, H. M.; Haszeldine, R. N.; Mather, A. P.; Parish, R. V. *J. Organomet. Chem.* **1978**, *161*, 91.

[4] Brady, K. A.; Nile, T. A. *J. Organomet. Chem.* **1981**, *206*, 299.

[5] Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. *Organometallics* **1990**, *9*, 3127.

[6] Ojima, I.; Donovan, R. J.; Clos, N. *Organometallics* **1991**, *10*, 2606.

[7] Ojima, I.; Ingallina, P.; Donovan, R. J.; Clos, N. *Organometallics* **1991**, *10*, 38.

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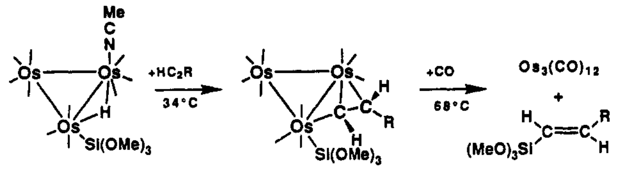
Scheme I



1a **2a**, R = Bu^t

that complex **1a** reacts readily with the terminal alkynes HC_2R (R = Bu^t, *p*-tolyl) to yield intermediate species that upon treatment with CO at 68 °C produce the silylolefins *trans*-R(H)C=C(H)Si(OMe)$_3$ (R = Bu^t, *p*-tolyl).[10] One of these intermediates, $Os_3(CO)_{10}[Si(OR)_3][\mu\text{-}C(H)C(H)\text{-}Bu^t]$ (**2a**; R = Me) has been isolated and structurally characterized by X-ray diffraction methods.[11,12] An ORTEP diagram of its molecular structure is shown in Figure 1. The molecule consists of a triosmium cluster with a bridging η^2-*tert*-butylvinyl ligand and a terminally coordinated trimethoxysilyl group positioned cis to the bridging carbon atom of the *tert*-butylvinyl group. The Os–Si distance is slightly longer than that in **1b**, 2.427 (4) vs 2.39 (1) Å.[8] The coordination of the bridging η^2-*tert*-butylvinyl ligand is structurally similar to that which has been reported for other osmium cluster complexes.[13] The trans stereochemistry of the hydrogen atoms is similar to that observed for the insertion of alkynes into the metal–hydrogen bonds of triosmium cluster complexes.[13d,14] The salient features of this study are (1) it is the hydrogen atom that is shifted first to the alkyne and (2) the silyl group is positioned adjacent to the bridging carbon atom of the bridging η^2-*tert*-butylvinyl ligand. This latter feature should and does facilitate the reductive-elimination step that is promoted by the CO addition and leads to the formation of the silicon–carbon bond (see Scheme I).

This is to our knowledge the first example of the isolation and structural characterization of an intermediate in an alkyne-hydrosilation reaction. Its isolation was made possible, no doubt, by the stabilization of the complex through the formation of the bridging alkenyl ligand. Efforts to produce a catalytic reaction by the addition of alkynes and silanes to **2** have not yet been successful. Silyl-containing triruthenium complexes have been implicated in the catalytic hydrosilation and silacarbonylation of olefins by $[Ru_3(CO)_{11}(\mu\text{-}H)]^-$.[15]

Acknowledgment. This research was supported by the National Science Foundation.

Registry No. **1a**, 131005-97-5; **2a**, 137540-21-7; **2b**, 137515-98-1; HC_2Bu^t, 917-92-0; HC_2-*p*-tolyl, 766-97-2; *trans*-(MeO)$_3$SiC(H)=C(H)Bu^t, 137515-96-9; *trans*-(MeO)$_3$SiC(H)=C(H)(*p*-tolyl), 137515-97-0.

Supplementary Material Available: Tables of crystal data, positional parameters, bond distances and angles, and anisotropic thermal parameters (10 pages); a table of structure factors (19 pages). Ordering information is given on any current masthead page.

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[8] Adams, R. D.; Cortopassi, J. E.; Pompeo, M. P. *Inorg. Chem.* **1991**, *30*, 2960.

[9] Compound **1a** was prepared by a procedure analogous to that used for the preparation of **1b**.[8] Analytical data for **1a**: IR (ν_{CO}, cm^{-1}; in hexane) 2104 (m), 2066 (vs), 2042 (vs), 2022 (vs), 2009 (s), 2001 (vs), 1989 (vs), 1977 (m); ^{1}H NMR (δ; in $CDCl_3$) 3.61 (s, O*CH*$_3$, 9 H), 2.59 (s, NC*CH*$_3$, 3 H), −16.57 (s, Os*H*, 1 H).

[10] A 51.5-mg (0.051-mmol) amount of **1a** was allowed to react with 0.10 mL of *tert*-butylacetylene in 50 mL of CH_2Cl_2 at 34 °C for 4.5 h. The product was separated from unreacted **1a** by TLC using a 2/1 (v/v) hexane/methylene chloride mixture as the eluent. This yielded red $Os_3(CO)_{10}[Si(OMe)_3][\mu\text{-}C(H)C(H)Bu^t]$ (**2a**; 13.0 mg, 0.012 mmol, 43% yield based on amount of **1a** consumed) and 23.0 mg of unreacted **1a**. Longer reaction times led to decomposition of the product and a decrease in the overall yield. Analytical data for **2a**: IR (ν_{CO}, cm^{-1}; in hexane) 2116 (s), 2066 (s), 2049 (vs), 2030 (vs), 2016 (s), 1996 (m), 1992 (m), 1977 (m), 1965 (s); ^{1}H NMR (δ; in $CDCl_3$) 9.33 (d, *CH*, $^3J_{HH}$ = 12.7 Hz, 1 H), 4.29 (d, *CH*, $^3J_{HH}$ = 12.7 Hz, 1 H), 3.60 (s, O*CH*$_3$, 9 H), 1.07 (s, *CH*$_3$, 9 H). Anal. Calcd for **2a**·C_5H_{12}: C, 25.6; H, 2.86. Found: C, 25.5; H, 2.54. $Os_3(CO)_{10}[Si(OR)_3][\mu\text{-}C(H)C(H)(p\text{-tolyl})]$ (**2b**) was obtained from **1a** by a similar treatment using HC_2-*p*-tolyl. Analytical data for **2b**: IR (ν_{CO}, cm^{-1}; in hexane) 2116 (s), 2067 (s), 2049 (vs), 2031 (vs), 2021 (s), 1999 (m), 1992 (m), 1978 (m), 1971 (s); ^{1}H NMR (δ; in $CDCl_3$) 9.76 (d, *CH*, $^3J_{HH}$ = 12.6 Hz, 1 H), 7.18 (d, C_6H_4, 2 H), 7.10 (d, C_6H_4, 2 H), 5.16 (d, *CH*, $^3J_{HH}$ = 12.6 Hz, 1 H), 3.55 (s, O*CH*$_3$, 9 H), 2.33 (s, *CH*$_3$, 3 H). A 50-mL solution of hexane containing 13.9 mg (0.013 mmol) of **2a** was refluxed for 5 h under a CO atmosphere. An aliquot of this solution was then removed and distilled at 50 °C and 0.5 mmHg pressure. A GC/MS analysis of this sample showed the peaks expected for (MeO)$_3$SiC(H)=C(H)Bu^t (*m/e* (%)): [M$^+$] 204 (3.2), 172 (2.8), 157 (5.2), 147 (0.4), 121 (100.0), 91 (34.8), 82 (28.0). ^{1}H NMR (δ; in $CDCl_3$): 6.44 (d, *CH*, $^3J_{HH}$ = 19.3 Hz, 1 H), 5.26 (d, *CH*, $^3J_{HH}$ = 19.3 Hz, 1 H), 3.55 (s, O*CH*$_3$, 9 H), 1.01 (s, *CH*$_3$ 9 H). The $^3J_{HH}$ coupling constants of the olefinic hydrogen atoms are indicative of the trans stereochemistry. Due to the small amount of material involved, an accurate amount of the olefin that was formed could not be determined; however, 8.2 mg of $Os_3(CO)_{12}$ (69% yield) coproduct was obtained. *trans*-(MeO)$_3$SiC(H)=C(H)(*p*-tolyl) was obtained similarly. ^{1}H NMR (δ; in $CDCl_3$): 7.36 (d, C_6H_4, 2 H), 7.16 (d, *CH*, $^3J_{HH}$ = 19.2 Hz, 1 H), 7.14 (d, C_6H_4, 2 H), 6.06 (d, *CH*, $^3J_{HH}$ = 19.3 Hz, 1 H), 3.60 (s, O*CH*$_3$, 9 H), 2.33 (s, *CH*$_3$, 3 H). Mass spectral analysis (*m/e* (%)): [M$^+$] 238 (42.2), 223 (31.4), 208 (23.0), 176 (53.9), 146 (12.3), 118 (100.0), 107 (24.9), 91 (72.0).

[11] Red crystals of **2a** were grown from a pentane solution by slow evaporation of solvent at 10 °C. Crystal data: space group $P2_1/a$, a = 13.309 (4) Å, b = 12.307 (4) Å, c = 17.499 (4) Å, β = 103.93 (2)°, Z = 4, 2711 reflections, R = 0.032.

[12] Diffraction measurements at 20 °C were made on a Rigaku AFC6S four-circle diffractometer using Mo Kα radiation. The structure solution and refinement was made by using the TEXSAN structure-solving program library (version 5.0) of the Molecular Structure Corp., The Woodlands, TX. An absorption correction was applied to the data.

[13] (a) Orpen, A. G.; Pippard, D.; Sheldrick, G. M.; Rouse, K. D. *Acta Crystallogr.* **1978**, *B34*, 2466. (b) Guy, J. J.; Reichert, B. E.; Sheldrick, G. M. *Acta Crystallogr.* **1976**, *B32*, 3319. (c) Sappa, E.; Tiripicchio, A.; Manotti Lanfredi, A. M. *J. Organomet. Chem.* **1983**, *249*, 391. (d) Clauss, A. D.; Tachikawa, J. R.; Pierpont, C. G. *Inorg. Chem.* **1981**, *20*, 1528.

[14] Deeming, A. J. *Adv. Organomet. Chem.* **1986**, *26*, 1 and references therein.

[15] Süss-Fink, G.; Reiner, J. *J. Mol. Catal.* **1982**, *16*, 231.

Unusual Selective α-Fission of Indium–*sec*-Alkyl Bonds in Solution

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Summary: Indium trialkyls possessing an α-branch such as In(Bu-*s*)$_3$ and In(Pr-*i*)$_3$ decompose through α-fission to give the corresponding alkyl radical selectively during solution pyrolysis.

Increasing attention has been paid to organometallic sources, as an innovative materials in the process for VLSI and the preparation of alloy semiconductors. Since it is important to lower the deposition temperature and to increase the purity of the layer for the production of high-performance and high-reliability devices, understanding the thermal decomposition path of the organo-

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