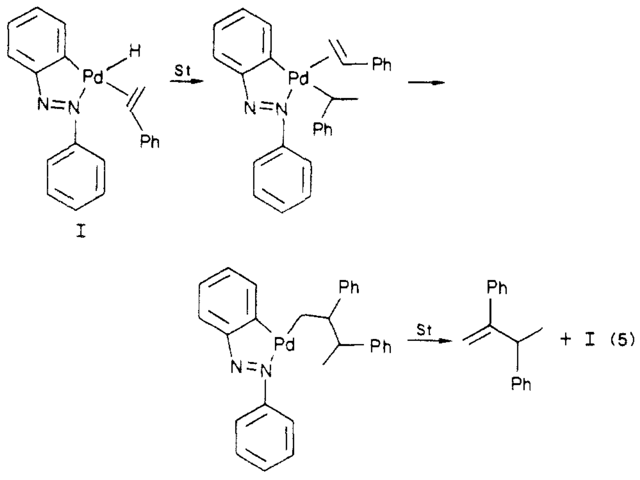

St = styrene

phosphine $\pi$-allylic palladium(II) chloride[12] dimerize styrene to 1,3-diphenyl-1-butene.

We are currently studying the scope of the alkyne and alkene reactions with various cyclopalladated complexes.

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(12) Grenouillet, P.; Neibecker, D.; Tkatchenko, I. *Organometallics* **1984,** *3,* 1130.

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# Novel Ligand Transformations in Cluster Complexes. $\alpha$-CH Bond Activation in a Secondary Carbene Ligand in a Triosmium Cluster

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*Summary:* The carbene cluster complex $Os_3(CO)_9[C(H)NMe_2](\mu\text{-}SPh)(\mu\text{-}H)$ **(2)** has been synthesized in 66% yield by the reaction of $Os_3(CO)_{10}(\mu\text{-}SPh)(\mu\text{-}H)$ with $CH_2(NMe_2)_2$. Photodecarbonylation of **2** leads to formation of the compound $Os_3(CO)_8(\mu\text{-}C{=}NMe_2)(\mu\text{-}SPh)(\mu\text{-}H)$ **(3)** in 37% yield by an $\alpha$-CH bond activation in the carbene ligand.

The ability of transition-metal cluster compounds to produce transformations in small molecules by interactions at two or more metal sites has been one of the most exciting and important aspects of the chemistry of these compounds.[1] The intramolecular activation of C–H bonds by clusters is a topic that has received considerable attention.[2] An understanding of these transformations in clusters could play an important role in developing a unified understanding of Fischer–Tropsch and related catalytic processes.[3] We have recently reported that the cluster $Os_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ reacts with trimethylamine at 125 °C to activate two C–H bonds on one of the methyl groups to form the new cluster $Os_3(CO)_8[C(H)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ (1) which contains a secondary (dimethylamino)carbene ligand.[4] We have now found that $Os_3(CO)_{10}(\mu\text{-}SPh)(\mu\text{-}H)$ reacts with bis(dimethylamino)methane to yield the new carbene cluster complex $Os_3(CO)_9[C(H)NMe_2](\mu\text{-}SPh)(\mu\text{-}H)$ (2) which upon photoinduced decarbonylation undergoes an intramolecular $\alpha$-CH bond activation that transforms the terminally coordinated carbene ligand into a bridging (dimethylamino)carbyne ligand.

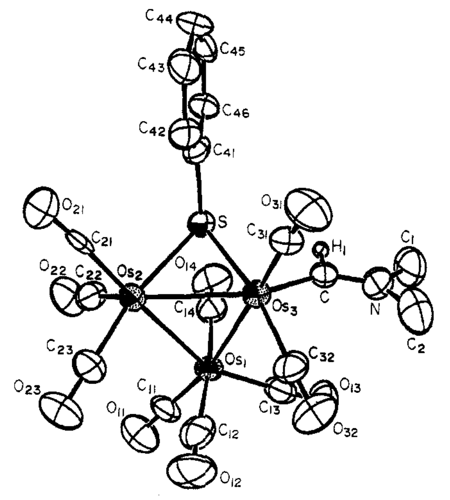

**Figure 1.** An ORTEP diagram of $Os_3(CO)_9[C(H)NMe_2](\mu\text{-}SPh)(\mu\text{-}H)$ (2) showing 50% probability thermal ellipsoids. The hydrogen atom H(1) is shown with an arbitrarily assigned temperature factor of $B = 1.0$ Å$^2$.

The reaction of 100 mg of $Os_3(CO)_{10}(\mu\text{-}SPh)(\mu\text{-}H)$ with 3.5 mL of $CH_2(NMe_2)_2$ in 100 mL of heptane solvent for 11 h at reflux yields 39 mg (66% based on the amount of $Os_3(CO)_{10}(\mu\text{-}SPh)(\mu_3\text{-}H)$ consumed) of compound 2. Compound 2 was characterized by IR and $^1H$ NMR spectroscopies and elemental and single-crystal X-ray diffraction analyses.[5-7] An ORTEP diagram of the molecular structure of 2 is shown in Figure 1.[8] The molecule consists of a triangular cluster of three osmium atoms that has one edge bridged by a phenylthio ligand. A hydride ligand (not observed crystallographically) is believed to bridge the Os(2)–Os(3) bond on the side of the cluster opposite

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(1) Adams, R. D.; Horvath, I. T. *Prog. Inorg. Chem.* **1985,** *33,* 127.

(2) (a) Cree-Uchiyama, M.; Shapley, J. R.; St. George, G. M. *J. Am. Chem. Soc.* **1986,** *108,* 1316. (b) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978,** *100,* 7726. (c) Green, M.; Hankey, D. R.; Murray, M.; Orpen, A. G.; Stone, *J. Chem. Soc., Chem. Commun.* **1981,** 689. (d) Tachikawa, M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1980,** *102,* 4542.

(3) (a) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979,** *79,* 479. (b) Brady, R. C.; Pettit, R. *J. Am. Chem. Soc.* **1981,** *103,* 1297; **1980,** *102,* 6181. (c) Biloen, P; Helle, H. N.; Sachtler, W. M. H. *J. Catal.* **1979,** *58,* 95.

(4) Adams, R. D.; Kim, H. S.; Wang, S. *J. Am. Chem. Soc.* **1985,** *107,* 6107.

(5) Compound **2** is air-stable and was isolated by TLC on silica gel using a 10:90 $CH_2Cl_2$/hexane solvent mixture. IR in hexane solvent ($\nu$(CO), cm$^{-1}$): 2092 (m), 2052 (m), 2013 (vs), 2002 (w), 1996 (m), 1966 (w), 1940 (w). $^1H$ NMR ($CD_2Cl_2$, $\delta$): 11.71 (s, 1 H), 7.22 (m, 5 H), 3.61 (s, 3 H), 3.56 (s, 3 H), −17.24 (s, 1 H). Elemental Anal. Calcd (Found): C, 21.80 (21.91); H, 1.32 (1.31); N, 1.41 (1.42).

(6) Diffraction measurements were made on a Rigaku AFC6 automatic diffractometer by using Mo K$\bar{\alpha}$ radiation. Structure solutions and refinements were performed on a Digital Equipment Corp. MICROVAX I computer by using the Molecular Structure Corp. TEXSAN program library. The data were corrected for absorption.

(7) Crystals of **2** were grown by slow evaporation of solvent from $CH_2Cl_2$/hexane solutions at −20 °C. Compound **2** crystallizes in the monoclinic crystal system: space group $P2_1/n$, $a = 15.841$ (3) Å, $b = 10.246$ (2) Å, $c = 15.594$ (3) Å, $\beta = 111.23$ (1)°, $Z = 4$, $\rho_{\text{calcd}} = 2.58$ g/cm$^3$. The structure was solved by direct methods (MULTAN) and was refined (2800 reflections) to the final values of the residuals $R = 0.0357$ and $R_w = 0.0435$.

(8) Selected interatomic distances (Å) and angles (deg) for **2** are as follows: Os(1)–Os(2) = 2.8711 (9), Os(1)–Os(3) = 2.877 (1), Os(2)–Os(3) = 2.8640 (9), Os(3)–C = 2.02 (2), C–N = 1.28 (2), C–H(1) = 1.06; Os(1)–Os(3)–C = 93.6 (4), Os(2)–Os(3)–C = 135.1 (4), Os(3)–C–N = 137 (1).

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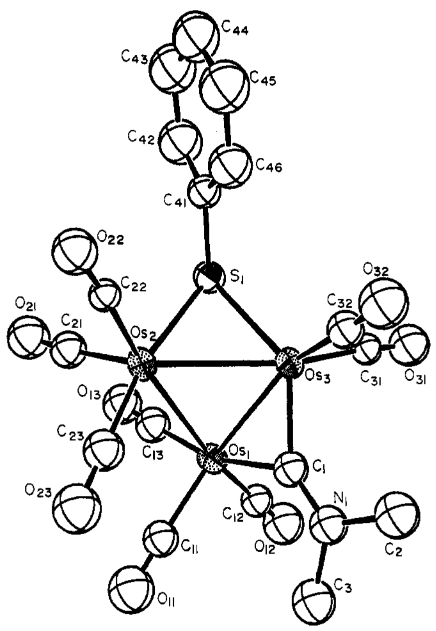
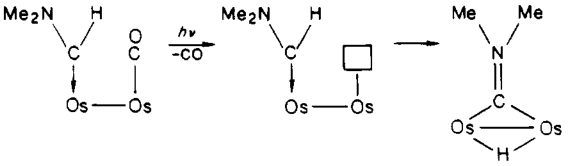


**Figure 2.** An ORTEP diagram of one of the two crystallographically independent molecules of $Os_3(CO)_8(\mu\text{-}C{=}NMe_2)(\mu\text{-}SPh)(\mu\text{-}H)_2$ (3) showing 50% probability thermal ellipsoids.

**Scheme I**



that of the phenylthio ligand. A secondary (dimethylamino)carbene ligand, $C(H)NMe_2$, is terminally coordinated to Os(3). The Os(3)–C (carbene) distance of 2.02 (2) Å is essentially the same as the osmium–carbon distance of 2.026 (15) Å [2.04 (2) Å] found to the carbene ligand in 1.[4] The C–N distance of 1.28 (2) Å and the Os(3)–C–N angle of 137 (1)° are also very similar to the corresponding dimensions of the carbene ligand in 1, 1.27 (2) Å [1.26 (2) Å] and 135 (1)° [136 (1)°]. The hydrogen atom on the carbene carbon atom was located in a difference Fourier synthesis, C–H = 1.06 Å, but the refinement of its position was not attempted. This hydrogen atom exhibits the characteristic low-field $^1H$ NMR shift (11.71 ppm) of secondary carbene ligands.[4,9]

When 40 mg of 2, dissolved in 100 mL of $C_6H_{12}$ solvent, was subjected to UV irradiation (high-pressure Hg arc) for 30 min, it was decarbonylated and transformed into $Os_3(CO)_8(\mu\text{-}C{=}NMe_2)(\mu\text{-}SPh)(\mu\text{-}H)_2$ (3, 15 mg, 37% yield). Compound 3 was characterized by IR and $^1H$ NMR spectroscopies and elemental and single-crystal X-ray diffraction analyses.[6,10,11] The compound crystallizes with two symmetry-independent molecules in the asymmetric crystal unit. Both molecules are structurally similar, and an ORTEP diagram of one of these is shown in Figure 2. The molecule consists of a triangular cluster of three osmium atoms that has one edge bridged by a phenylthio ligand. There are two inequivalent bridging hydride ligands ($^1H$ NMR δ −13.71 (s), −15.84 (s)) that were not observed crystallographically. The most interesting ligand is a (dimethylamino)carbyne ligand that bridges the Os(1)–Os(3) edge of the cluster. The bonding of the carbon atom to the metal atoms is slightly asymmetric, Os(1A)–C(1A) = 2.12 (2) Å [Os(1B)–C(1B) = 2.10 (2) Å] vs. Os(3A)–C(1A) = 2.00 (2) Å [Os(3B)–C(1B) = 2.00 (2) Å], and there is multiple bonding between the carbon and nitrogen atoms, C(1A)–N(1A) = 1.27 (3) Å [C(1B)–N(1B) = 1.32 (3) Å]. Bridging (dialkylamino)carbyne ligands have been prepared by other methods,[13] but this report documents the first example of one formed by an intramolecular carbene–carbyne transformation that is ostensibly binuclear in nature.[14]

Mechanistically, it is believed that the photoinduced decarbonylation of 2 occurs at the CO-rich $Os(CO)_4$ group adjacent to the coordination site of the carbene ligand, Os(3). An oxidative addition of the C–H bond then occurs at the vacant site, and this leads directly to the formation of the bridging carbyne ligand; see Scheme I.

Lewis acid promoted transformations of heteronuclear carbene ligands into carbyne ligands are well-established reactions,[16] but these reactions differ significantly from the one reported here. In the Lewis acid promoted transformations it is the heteronuclear C–X (X = OR, $NR_2$, Cl, etc. bond that is cleaved.[16] In this reaction the heteronuclear C–N bond is retained.

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**Supplementary Material Available:** Tables of fractional atomic coordinates and thermal parameters and selected interatomic distances and angles (13 pages); listings of structure factor amplitudes (51 pages). Ordering information is given on any current masthead page.

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(9) (a) Hartshorn, A. J.; Lappert, M. F.; Turner, K. *J. Chem. Soc., Dalton Trans.* **1978**, *348*. (b) Cutler, A. *J. Am. Chem. Soc.* **1979**, *101*, 604. (c) Yu, Y. S.; Angelici, R. *Organometallics* **1983**, *2*, 1018.

(10) Compound 3 is air-stable and was isolated by TLC on silica gel using a 40:60 $CH_2Cl_2$/hexane solvent mixture. IR in hexane solvent (ν(CO), $cm^{-1}$): 2086 (m), 2050 (vs), 2020 (s), 2012 (s), 1999 (w), 1990 (m), 1975 (w), 1953 (m), $^1H$ NMR ($CD_2Cl_2$ δ): 7.30 (m, 5 H), 4.01 (s, 3 H), 3.85 (s, 3 H), −13.71 (s, 1 H), −15.84 (s, 1 H). Elemental Anal. Calcd (Found): C, 21.21 (21.15); H, 1.36 (1.29); N, 1.46 (1.36).

(11) Crystals of 3 were grown by slow evaporation of solutions in benzene solvent at 25 °C. Compound 3 crystallized in the triclinic crystal system: space group $P\bar{1}$, $a = 9.278$ (1) Å, $b = 32.668$ (5) Å, $c = 7.644$ (1)°, $\alpha = 90.26$ (1)°, $\beta = 99.99$ (1)°, $\gamma = 96.07$ (1)°, $Z = 4$, $\rho_{calcd} = 2.82$ g/cm$^3$. The structure was solved by a combination of Patterson and difference Fourier techniques and was refined (4616 reflections) to the final values of the residuals $R = 0.0530$ and $R_w = 0.0588$.

(12) There are two symmetry-independent molecules in the asymmetric crystal unit. Selected interatomic distances (Å) and angles (deg) are as follows, (the values in brackets correspond to the second molecule): Os(1A)–Os(2A) = 2.942 (2), [Os(1B)–Os(2B) = 2.933 (1)], Os(1A)–Os(3A) = 2.791 (1), [Os(1B)–Os(3B) = 2.794 (1)], Os(2A)–Os(3A) = 2.842 (1), [Os(2B)–Os(3B) = 2.850 (1)], Os(1A)–C(1A) = 2.12 (2), [Os(1B)–C(1B) = 2.10 (2)], Os(3A)–C(1A) = 2.00 (2), [Os(3B)–C(1B) = 2.00 (2)], C(1A–N(1A) = 1.27 (3), [C(1B)–N(1B) = 1.32 (3)]; Os(1A–C(1A)–N(1A) = 136 (2), [Os(1B)–C(1B)–N(1B) = 135 (2)], Os(3A)–C(1A)–N(1A) = 138 (2), [Os(3B)–C(1B)–N(1B) = 139 (2).

(13) (a) Keister, J. B.; Horling, T. L. *Inorg. Chem.* **1980**, *19*, 2304. (b) Churchill, M. R.; DeBoer, B. G.; Rotella, F. J. *Inorg. Chem.* **1976**, *15*, 1843. (c) Yin, C. C.; Deeming, A. J. *J. Organomet. Chem.* **1977**, *133*, 123.

(14) Carbene–carbyne transformations that involve cleavage of the C–X bond have been observed in the mononuclear complexes $Cr(CO)_5$-[$C(X)NEt_2$], but these transformations are as yet restricted to the cases where X = Cl,[15a] Br, I,[15b] $SnPh_3$,[15c] $SeC_6H_4R$,[15b] $PbPh_3$,[15e] and TePh.[15f]

(15) (a) Fischer, H.; Motsch, A.; Kleine, W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 842. (b) Fischer, E. O.; Kleine, W.; Kreissl, F. R.; Fischer, H.; Friedrich, P.; Huttner, G. *J. Organomet. Chem.* **1977**, *128*, C49. (c) Fischer, E. O.; Fischer, H.; Schubert, U.; Pardy, R. B. A. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 871. (d) Fischer, E. O.; Himmelreich, D.; Cai, R.; Fischer, H.; Schubert, U.; Zimmer-Gasser, B. *Chem. Ber.* **1981**, *114*, 3209. (e) Fischer, H.; Fischer, E. O.; Cai, R. *Chem. Ber.* **1982**, *115*, 2707. (f) Fischer, H.; Fischer, E. O.; Cai, R.; Himmelreich, P. *Chem. Ber.* **1983**, *116*, 1009.

(16) Kreissl, F. R. In *Transition Metal Carbene Complexes*, Verlag Chemie: Weinheim, 1983, and references therein.