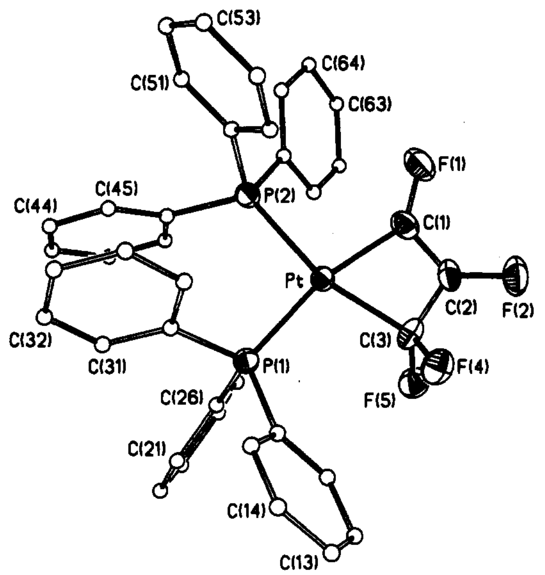


Figure 1. Molecular structure of complex **4a**. Carbon atoms in the phenyl rings are shown as spheres of arbitrary radius.

Table II. Selected Bond Lengths and Angles for Complex 4a

Selected Bond Lengths (Å)	
Pt-P(1) 2.302 (2)	Pt-P(2) 2.336 (2)
Pt-C(1) 2.039(9)	Pt-C(3) 2.079 (8)
C(1)-C(2) 1.351 (12)	C(2)-C(3) 1.474 (12)
C(1)-F(1) 1.325 (10)	C(2)-F(2) 1.373 (11)
C(3)-F(4) 1.371 (8)	C(3)-F(5) 1.414 (9)
Selected Bond Angles (deg)	
P(1)-Pt-P(2) 98.8 (1)	Pt-C(1)-C(2) 97.5 (6)
P(1)-Pt-C(1) 165.2 (2)	Pt-C(1)-F(1) 138.0 (6)
P(1)-Pt-C(3) 99.6 (2)	Pt-C(3)-C(2) 92.0 (5)
P(2)-Pt-C(1) 96.0 (2)	Pt-C(3)-F(4) 123.6 (5)
P(2)-Pt-C(3) 160.6 (2)	Pt-C(3)-F(5) 115.6 (5)
C(1)-Pt-C(3) 65.8 (3)	C(1)-C(2)-C(3) 104.7 (7)
F(1)-C(1)-C(2) 124.5 (8)	F(2)-C(2)-C(1) 130.5 (8)
F(2)-C(2)-C(3) 124.8 (7)	F(5)-C(3)-C(2) 111.0 (6)
F(4)-C(3)-C(2) 112.5 (6)	F(4)-C(3)-F(5) 102.1 (6)

The molecular structure of **4a** is shown in Figure 1. Fractional atomic coordinates are presented in Table I, and selected bond lengths and angles are assembled in Table II. The metallacyclobutene ring is planar, with no atom deviating more than 0.015 Å from the plane. There is a significant deviation from planarity in the coordination sphere of platinum, the metallacyclobutene plane being canted by 7.6° from the P(1)-Pt-P(2) plane. Similar deviations from planarity within the coordination sphere of the metal have been noted in saturated platinacyclobutanes, though the metallacyclobutane rings themselves in these Pt(II) derivatives are usually found to be puckered.[35] The distance from Pt to the formally sp^2 C(1) is significantly shorter than that to the sp^3 C(3), but the higher trans-influence of the sp^3 carbon is implied by the significantly longer distance from Pt to P(2) compared to that to P(1). Identical trends in M-C and M-P distances are found in the octahedral iridium(III) metallacyclobutene complex **5**.[27] Complexes **4** represent the first examples of the smallest unsaturated perfluorinated metallacycle, although a fully saturated perfluorometallacyclobutane complex of iron has been prepared and crystallographically characterized.[37]

The solution structures of **4a** and **4b** were shown by $^{19}F\{^{31}P\}$, $^{19}F\{^{19}F\}$, and $^{31}P\{^1H\}$ NMR spectroscopic methods[33] to be analogous to that observed for **4a** in the solid state. Observation of three resonances of relative intensity 2:1:1 in the ^{19}F NMR spectrum of **4a**, even at -78 °C, illustrates that the metallacyclobutene structure is maintained in solution and that the solid-state distortion from planarity at Pt, which should result in different chemical shifts for the fluorines in the CF_2 group, cannot be frozen out in solution. The different trans influence of the metallacyclobutene carbon atoms results in significantly different values for J_{Pt-P} in both **4a** and **4b**.

Finally we note that formation of complexes **4** via C-C bond cleavage demonstrates the high reactivity of perfluorocyclopropene compared to both its fluorinated homologues and its hydrocarbon analogues. While perfluorocyclobutene forms a simple η^2-olefin complex **6** with Pt(0),[36] we have been unable to observe formation of the cyclopropene analogue at low temperatures, even though hydrocarbon cyclopropenes form stable η^2-olefin complexes with Pt(0).[10,11] We cannot distinguish whether the metallacyclobutene compounds **4** are formed via an intermediate η^2-olefin complex or via direct attack of the metal at a C-C bond.

Acknowledgment. We are grateful to the Air Force Office of Scientific Research (Grant AFOSR-86-0075) and the National Science Foundation for generous support of our research. A generous loan of K_2PtCl_4 from Matthey-Bishop Inc. is also gratefully acknowledged.

Supplementary Material Available: Tables of bond distances and angles, anisotropic thermal parameters, and hydrogen-atom coordinates (4 pages); a listing of observed vs calculated structure factors (24 pages). Ordering information is given on any current masthead page.

---

[35] Yarrow, D. J.; Ibers, J. A.; Lenarda, M.; Graziani, M. *J. Organomet. Chem.* **1974**, *70*, 133-145. Rajaram, J.; Ibers, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 829-838. Ibers, J. A.; DiCosimo, R.; Whitesides, G. M. *Organometallics* **1982**, *1*, 13-20. Klingler, R. J.; Huffman, J. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 2147-2157.

[36] Green, M.; Osborn, R. B. L.; Rest, A. J.; Stone, F. G. A. *J. Chem. Soc. A* **1968**, 2525-2530.

[37] Ittel, S. D.; Karel, K.; Tulip, T. H., submitted for publication.

Clusters Containing Carbene Ligands. The Unusual Synthesis, Coordination, and Reactivity of a Bridging (Dimetalliomethyl)(diethylamino)carbene Ligand in the Cluster Complex $Os_3(CO)_9[\mu_3\text{-}HCC(NEt_2)](\mu\text{-}H)_2$

Richard D. Adams* and James T. Tanner

Department of Chemistry, University of South Carolina
Columbia, South Carolina 29208

Received July 29, 1988

Summary: The photoinduced decarbonylation of $Os_3(CO)_{10}[\mu\text{-}C(H)C(H)NEt_2](\mu\text{-}H)$ (**1**) yields $Os_3(CO)_9[\mu_3\text{-}CC(H)NEt_2](\mu\text{-}H)_2$ (**2**; 58% yield) and $Os_3(CO)_9[\mu_3\text{-}C(H)CNEt_2](\mu\text{-}H)_2$ (**3**; 21% yield). Compound **3** was also obtained from **2** in 70% yield by heating to 68 °C in hexane solvent. Both products were characterized by IR, ^1H NMR, and X-ray diffraction analyses. Compound **2** contains an η^1-triply bridging (diethylamino)alkenylidene ligand coordinated to a triangular triosmium cluster. Compound **3** contains a triply bridging HC_2NEt_2 ligand that is formulated to include two osmiums as a (dimetalliomethyl)(diethylamino)carbene ligand on the basis of structural and reactivity evidence. Compound **3** reacts with $NHPr^n_2$ to yield $Os_3(CO)_9[\mu_3\text{-}C(H)CNPr^n_2](\mu\text{-}H)_2$ (**4**) in 74% yield by replacement of the diethylamino group.

0276-7333/88/2307-2241$01.50/0

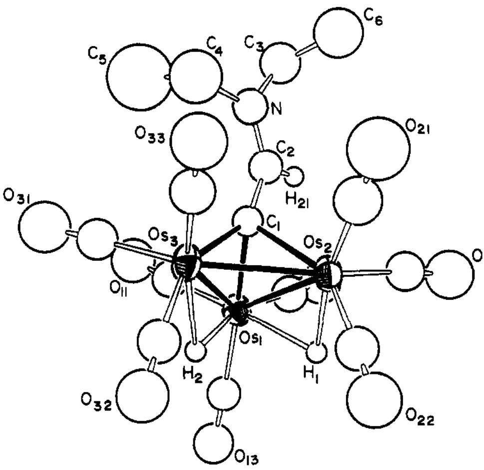


Figure 1. An ORTEP diagram of $Os_3(CO)_9[\mu_3\text{-}CC(H)NEt_2](\mu\text{-}H)_2$ (2) showing 50% probability thermal ellipsoids.

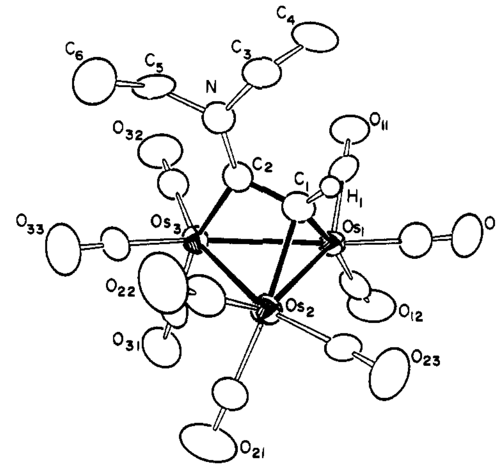
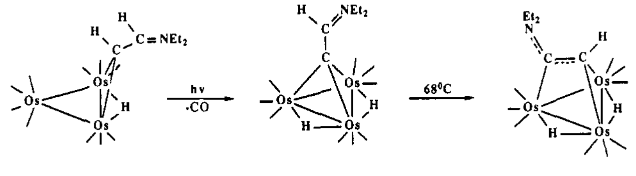


Figure 2. An ORTEP diagram of $Os_3(CO)_9[\mu_3\text{-}HCC(NEt_2)](\mu\text{-}H)_2$ (3) showing 50% probability thermal ellipsoids.

Metal complexes containing heteronuclear carbenes have been a source of great interest both for their unusual structural varieties and reactivities and for their applications to novel organic syntheses.[1,2] While the study of mononuclear metal complexes containing carbene ligands has been extensive, the study of carbene ligands in cluster complexes has begun only recently.[3] The paucity of cluster complexes containing carbene ligands may be due to the very limited success of the traditional methods of syntheses.[3b,c,f] Recently, we have shown that cluster complexes containing secondary (dialkylamino)carbene ligands can be prepared by C–H activation reactions of NMe_3 and bis(dialkylamino)methanes, $CH_2(NR_2)_2$, with certain osmium cluster complexes.[4] In an extension of these studies, we now wish to report the synthesis and characterization of a new cluster complex that appears to contain the first example of a dimetalated methyl(diethylamino)carbene ligand.

UV irradiation of the complex $Os_3(CO)_{10}[\mu\text{-}C(H)C(H)NEt_2](\mu\text{-}H)$ (1)[5] leads to decarbonylation and formation of the isomeric complexes $Os_3(CO)_9[\mu_3\text{-}CC(H)NEt_2](\mu\text{-}H)_2$ (2) in 58% yield and $Os_3(CO)_9[\mu_3\text{-}C(H)CNEt_2](\mu\text{-}H)_2$ (3) in 21% yield.[6] Compound 3 was obtained directly from 2 in 70% yield by heating to 68 °C for 3 h. Both compounds have been characterized by X-ray crystallographic methods.[7] An ORTEP drawing of 2 is shown in Figure 1.[8] Compound 2 contains a triangular triosmium cluster with a triply bridging $CC(H)NEt_2$ ligand that is bonded to the metal atoms only by the carbon C(1). Carbon C(2) contains only three substituents, but the short C(1)–C(2) and C(2)–N distances of 1.39 (2) and 1.31 (2) Å indicate the existence of partial multiple-bonding characters. In addition, the ethyl groups are inequivalent due to hindered rotation about the C(2)–N bond and the nitrogen atom possesses a planar geometry. The ligand could be viewed as a (diethylamino)alkenylidene ligand in a novel η^1-co-

Scheme I



1 2 3

---

(1) (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Chemistry*; Verlag Chemie: Weinheim, West Germany, 1983. (b) Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1.

(2) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Transition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 16. (b) Dötz, K. H. *J. Organomet. Chem.* **1987**, *334*, 57. (c) Chan, K. S.; Peterson, G. A.; Brandvold, T. A.; Faron, K. L.; Challener, C. A.; Hyldahl, C.; Wulff, W. D. *J. Organomet. Chem.* **1987**, *334*, 9. (d) Dötz, K. H. *Pure Appl. Chem.* **1983**, *55*, 1689.

(3) (a) Ashworth, T. V.; Berry, M.; Howard, J. A. K.; Laguna, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1615. (b) Jensen, C. M.; Lynch, T. J.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1982**, *104*, 4679. (c) Jensen, C. M.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1984**, *106*, 5926. Jensen, C. M.; Kaesz, H. D. *J. Am. Chem. Soc.* **1983**, *105*, 6969. (e) Shapley, J. R.; Yeh, W. Y.; Churchill, M. R.; Li, Y. *Organometallics* **1985**, *4*, 1898. (f) Williams, G. D.; Geoffroy, G. L.; Whittle, R. R.; Rheingold, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 729. (g) Richmond, M. G.; Kochi, J. K. *Organometallics* **1987**, *6*, 777.

(4) (a) Adams, R. D.; Kim, H. S.; Wang, S. *J. Am. Chem. Soc.* **1985**, *107*, 6107. (b) Adams, R. D.; Babin, J. E.; Kim, H. S. *Inorg. Chem.* **1986**, *25*, 4319. (c) Adams, R. D.; Babin, J. E.; Kim, H. S. *J. Am. Chem. Soc.* **1987**, *109*, 1414. (d) Adams, R. D.; Babin, J. E. *Organometallics* **1987**, *6*, 1364. (e) Adams, R. D.; Babin, J. E. *Organometallics* **1988**, *7*, 963.

(5) Shapley, J. R.; Tachikawa, M.; Churchill, M. R.; Lashewycz, R. A. *J. Organomet. Chem.* **1978**, *162*, C39.

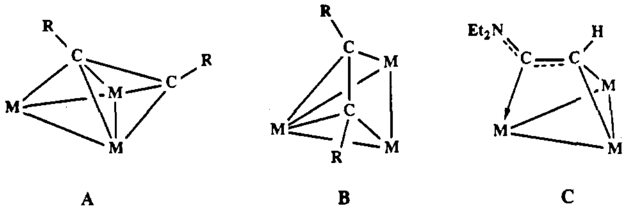
(6) 1 (100 mg) was dissolved in 100 mL of hexane and irradiated (UV external) for 2.5 h. The products 2 and 3 were isolated by TLC on silica gel using hexane/CH_2Cl_2 (8/2) solvent in 58% and 21% yields, respectively. 2 elutes more slowly than 3. For 2: ν(CO) in hexane, 2096 (m), 2064 (vs), 2037 (vs), 2018 (s), 2009 (m), 1982 (s), 1971 (m), 1957 (w) cm^{-1}; ^1H NMR (δ in $CDCl_3$ at 80 MHz) 9.10 (s, 1 H), 3.61 (q, 2 H, J = 7 Hz), 3.53 (q, 2 H, J = 7 Hz), 1.28 (t, 6 H, J = 7 Hz), −19.31 (s, 2 H). For 3: ν(CO) in hexane, 2101 (s), 2071 (vs), 2045 (vs), 2018 (sh), 2015 (s), 2000 (s), 1982 (s), 1977 (w, sh), 1967 (m) cm^{-1}; ^1H NMR (δ in $CDCl_3$ at 300 MHz) 5.87 (s, 1 H), 3.91 (q, 2 H, J = 7 Hz), 3.54 (q, 2 H, J = 7 Hz), 1.28 (t, 3 H, J = 7 Hz), 1.22 (t, 3 H, J = 7 Hz), −16.35 (s, br, 1 H), −18.90 (s, br, 1 H). A 102 °C, 80 MHz in toluene-d_8, the hydride resonances have coalesced to a singlet at −18.15 ppm, but there was no evidence of broadening of the resonances of the ethyl groups. When heated to reflux in hexane solvent, compound 2 was converted to 3 in 70% yield.

(7) Diffraction data were collected on a RIGAKU AFC6 automatic diffractometer using Mo Kα radiation. All calculations were performed on a Digital Equipment Corp. MICROVAX II computer using the TEXSAN structure solving program library (Version 2.0), obtained from the Molecular Structure Corp., College Station, TX. For 2: space group $P2_1/n$, a = 10.233 (2) Å, b = 14.834 (4) Å, c = 14.538 (2) Å, β = 99.88 (2)°, Z = 4. The structure was solved by direct methods and was refined (2403 reflections) to the final residuals R = 0.036 and R_w = 0.040. An analytical absorption correction was applied. For 3: space group $P2_1/a$, a = 12.616 (2) Å, b = 12.566 (3) Å, c = 13.706 (2) Å, β = 106.56 (1)°, Z = 4. The structure was solved by direct methods and was refined (1956 reflections) to the final values of the residuals, R = 0.035 and R_w = 0.036. An empirical absorption correction was applied.

(8) Selected intramolecular distances (Å) and angles (deg) or 2 are as follows: Os(1)–Os(2) = 2.852 (1), Os(1)–Os(3) = 2.864 (1), Os(2)–Os(3) = 2.756 (1), Os(1)–C(1) = 2.12 (1), Os(2)–C(1) = 2.15 (1), Os(3)–C(1) = 2.06 (1), C(1)–C(2) = 1.39 (2), C(2)–N = 1.31 (2), C(1)–C(2)–N = 133 (1).

ordination mode. There are two bridging hydride ligands as shown in Figure 1.

An ORTEP diagram of **3** is shown in Figure 2.[9] Compound **3** consists of a triangular triosmium cluster with a triply bridging HC_2NEt_2 ligand.[10,11] Although this ligand could be described formally as an "ynamine", for the reasons listed below, we feel that it is more appropriately described as a (dimetalliomethyl)(diethylamino) carbene ligand. The HC_2NEt_2 ligand in **3** differs from all other 48-electron trimetallic alkyne cluster complexes in that it possesses the μ_3-$\perp$ coordination mode A.[12] All the others



possess the μ_3-$\|$ mode B. The latter is observed in the very similar complex $Ru_3(CO_9(\mu_3\text{-}MeC_2OMe)(\mu\text{-}H)$ that was prepared by Keister.[11] The only examples of trimetallic clusters possessing the μ_3-$\perp$ mode are the 46-electron clusters $M_3(CO)_9(\mu_3\text{-}C_2Ph_2)$ (M_3 = Fe_3[14a] or Fe_2Ru[14b]), $W_2Fe(CO)_6Cp_2[\mu_3\text{-}C_2(p\text{-}tolyl)_2]$,[13] and $W_2Fe(CO)_5Cp_2(O)[\mu_3\text{-}C_2(p\text{-}tolyl)_2]$.[15] However, the coordination of the HC_2NEt_2 ligand **3** differs significantly from the 46-electron clusters with the μ_3-$\perp$ alkyne mode. In the latter examples, both alkyne carbon atoms are bonded to the $\perp$ edge of the cluster. In **3**, the ligand is shifted away from the $\perp$ edge toward the structure C. This is shown by the very long distances to C(2), Os(1)–C(2) = 2.91 (2) Å and Os(2)–C(2) = 2.80 (2) Å. We feel that the ligand in C can be described alternatively as a (dimetalliomethyl)(diethylamino)carbene. This formulation is also supported by the observation of the short C(2)–N distance of 1.33 (2) Å that is characteristic of aminocarbene ligands.[1] In addition, the nitrogen atom is planar and the ethyl groups are inequivalent (by ^1H NMR spectroscopy) due to the hindered rotation about the C(2)–N bond.[6] The two inequivalent hydride ligands (not observed crystallographically) are believed to bridge the Os(1)–Os(2) and Os(1)–Os(3) metal–metal bonds. Finally, it was found that the amino group in the HC_2NEt_2 ligand in **3** is readily exchanged by reaction with secondary amines as is also characteristic of carbene ligands.[1] The reaction of **3** with $NHPr^n_2$ at 97 °C gave the derivative $Os_3(CO)_9(\mu_3\text{-}HC_2NPr^n_2)(\mu\text{-}H)_2$ (**4**) in 74% yield.[16]

The transformation of **1** to **2** occurs presumably by a photoinduced decarbonylation at the $Os(CO)_4$ group and is followed by a C–H activation at the bridging carbon atom of the C(H)C(H)NEt_2 group; see Scheme I. This is probably similar to the transformation of $Os_3(CO)_{10}(\mu\text{-}CH_2)(\mu\text{-}H)_2$ to $Os_3(CO)_9(\mu_3\text{-}CH)(\mu\text{-}H)_3$.[17] Overall, the transformation of **2** to **3** involves a 1,2 shift of the hydrogen atom from C(2) to C(1). Mechanistically, this may involve a metal-promoted C–H activation with formation of an acetylide trihydride cluster intermediate that subsequently shifts a hydride ligand to the acetylide carbon to yield **3**. The reverse of this transformation (i.e. μ_3-alkyne to μ_3-alkenylidene) has been observed in other metal cluster complexes.[18]

The novel mode of coordination exhibited by the HC_2NEt_2 ligand in **3** can be attributed in part to the formation of C–N multiple bonding caused by donation from the lone pair of electrons on the nitrogen atom. This is more important than metal–carbon bonding, and the coordination mode C thus becomes more important than A. However, the novel reactivity of **3** is also directly dependent on the unique triply bridging coordination of the HC_2NEt_2 ligand. This example thus provides a further confirmation of the general principle that multicenter coordination can promote novel ligand reactivity.[19]

Acknowledgment. These studies were supported by the Office of Basic Energy Sciences of the U.S. Department of Energy. NMR measurements were made on a Brüker AM-300 spectrometer purchased with funds from the National Science Foundation under Grant No. CHE-8411172.

Supplementary Material Available: Tables of crystal data, fractional atomic coordinates, anisotropic thermal parameters, and selected interatomic distances and angles for both structural analyses (14 pages); listings of structure factor amplitudes (30 pages). Ordering information is given on any current masthead page.

---

[9] Selected intramolecular distances (Å) and angles (deg) for **3** are as follows: Os(1)–Os(2) = 2.832 (1), Os(1)–Os(3) = 3.003 (1), Os(2)–Os(3) = 2.802 (1), Os(1)–C(1) = 2.17 (2), Os(2)–C(1) = 2.14 (2), Os(1)–C(2) = 2.91 (2), Os(2)–C(2) = 2.80 (2), Os(3)–C(2) = 2.10 (2), C(1)–C(2) = 1.43 (2), C(2)–N = 1.33 (2); Os(3)–C(2)–N = 133, Os(3)–C(2)–C(1) = 105 (1), C(1)–C(2)–N = 121 (2).

[10] This compound was recently prepared by another route[11] but has not yet been characterized crystallographically.

[11] Boyar, E.; Deeming, A. J.; Kabir, S. E. *J. Chem. Soc., Chem. Commun.* **1986**, 577.

[12] Halet, J. F.; Saillard, J. Y.; Lissillor, R.; McGlinchey, M. J.; Jaouen, G. *Inorg. Chem.* **1985**, *24*, 218.

[13] Churchill, M. R.; Fettinger, J. C.; Keister, J. B.; See, R. F.; Ziller, J. W. *Organometallics* **1985**, *4*, 2112.

[14] (a) Blount, J. F.; Dahl, L. F.; Hoogzand, C.; Hübel, W. *J. Am. Chem. Soc.* **1966**, *88*, 292. (b) Busetti, V.; Granozzi, G.; Aime, S.; Gobetto, R.; Osella, D. *Organometallics* **1984**, *3*, 1510.

[15] Busetto, L.; Jeffrey, J. C.; Mills, R. M.; Stone, F. G. A.; Went, M.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1983**, 101.

[16] The reaction was performed in refluxing heptane solvent. for **4**, ν(CO) in hexane: 2101 (m), 2072 (vs), 2045 (vs), 2018 (sh), 2015 (vs), 2000 (s), 1982 (s), 1977 (w, sh), 1967 (m); ^1H NMR (δ in $CDCl_3$) 5.84 (s, 1 H), 3.48 (t, 2 H, J = 8 Hz), 3.40 (t, 2 H, J = 8 Hz), 1.66 (m, 4 H), 0.96 (t, 3 H, J = 6 Hz), 0.94 (t, 3 H, J = 7 Hz), −16.35 (s, br, 1 H), −18.90 (s, br, 1 H).

[17] Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5225.

[18] (a) von Schnering, C.; Albiez, T.; Bernhardt, W.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 479. (b) Roland, E.; Bernhardt, W.; Vahrenkamp, H. *Chem. Ber.* **1985**, *118*, 2858.

[19] (a) Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1976**, *85*, 451. (b) Adams, R. D.; Horvath, I. T. *Prog. Inorg. Chem.* **1985**, *33*, 127.

A Novel Dinuclear Tetrahydride-Bridged Ruthenium Complex, $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_4Ru(\eta^5\text{-}C_5Me_5)$

Hiroharu Suzuki,* Hideki Omori, Dong Hwan Lee, Yuka Yoshida, and Yoshihiko Moro-oka

Research Laboratory of Resources Utilization
Tokyo Institute of Technology, 4259 Nagatsuta
Midori-ku, Yokohama 227, Japan

Received June 15, 1988

Summary: The novel tetrahydride-bridged dinuclear ruthenium complex $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_4Ru(\eta^5\text{-}C_5Me_5)$ (**2**) has been synthesized by reaction of $[(\eta^5\text{-}C_5Me_5)RuCl_2]_n$ with $LiAlH_4$. X-ray crystal structure of complex **2** is reported.

Transition-metal hydrides are implicated in the variety of stoichiometric and catalytic organic transformations.[1] Di- and polyhydride complexes with electron-donating

---

[1] Muetterties, E. L., Ed. *Transition Metal Hydrides*; Marcel Dekker: New York, 1971.

0276-7333/88/2307-2243$01.50/0