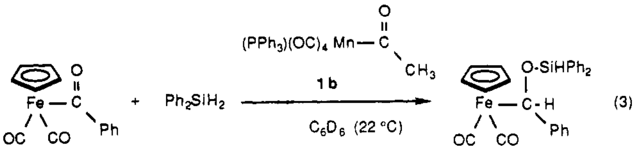
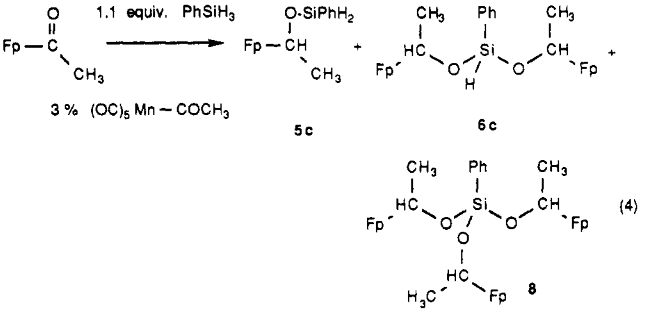
1b also is the most active manganese precatalyst thus far. It expedites the hydrosilation of $FpCOCH_3$ at less than 1% catalyst concentration and of FpCOPh (eq 3) under conditions that other manganese catalysts either are inert (**1a**) or react sluggishly (**2**).



7

Phenylsilane in the presence of **1a** also hydrosilates $FpCOCH_3$, but the final products are Fp(ethyl) and tris-Fp **8**. Treatment of a 1:1 mixture of $FpCOCH_3$ and $PhSiH_3$ with **1a** as the catalyst (4.6%, entry 18) in C_6D_6 quantitatively produces mixtures of mono-Fp **5c**, bis-Fp **6c**, and tris-Fp **8** α-siloxyethyl compounds within 8 h (eq 4); over an additional 4–6 h, **5c** and **6c** transform to Fp(ethyl). We assign structures **5c** and **6c** based on the close resemblance of their ^1H and ^{13}C NMR spectral data to that of the (diphenylsiloxy)ethyl compounds **5a** and **6a**. The fully characterized tris-Fp **8** and Fp(ethyl) are isolated by size exclusion chromatography, 26% and 53%, respectively.



Although manganese acyls **1a–c** and **2** are excellent catalysts, the presence of an acyl ligand is not a prerequisite for hydrosilation activity. Both $(CO)_5MnSiMe_3$ and $Mn_2(CO)_{10}$ function as relatively sluggish catalysts toward adding Ph_2SiH_2 (Table I) or Et_2SiH_2 to $FpCOCH_3$. The methyl complex $(CO)_5MnCH_3$, however, qualifies as a more reactive hydrosilation catalyst than **1a**, but it affords a lower **6a**/**5a** ratio of 0.23 that is comparable with those obtained from $(CO)_5MnSiMe_3$ and $Mn_2(CO)_{10}$. The siloxybenzyl compound $(CO)_5MnCHPh(OSiHPh_2)$,[9] which results from mixing **2** with Ph_2SiH_2 (3 min) before adding $FpCOCH_3$, is much less reactive than **2**, and yet it gives an equally high **6a**/**5a** ratio of 0.92.

Manganese alkyl and acyl complexes $L(CO)_4MnCOR$ are far more efficient catalysts than is $(PPh_3)_3RhCl$ for hydrosilating Fp(acetyl) and Fp(benzoyl). Studies in progress are extending their scope and investigating the mechanism[12] of these manganese-catalyzed hydrosilation reactions.

Acknowledgment. Support from the Department of Energy, Office of Basic Energy Science, is gratefully acknowledged.

Supplementary Material Available: Table 2, listing ^1H and ^{13}C NMR and IR spectral assignments for **3–7** and microanalytical data (3 pages). Ordering information is given on any current masthead page.

---

[12] We disfavor a pathway in which the manganese catalyst $Mn(CO)_5(COR)$ loses two terminal carbonyls in order to simultaneously bind silane and $FpCOCH_3$ as $(CO)_3(RCO)Mn(H)(SiR'_3)[O{=}C(CH_3)Fp]$. A plausible working hypothesis is a free-radical mechanism in which a 17-electron species $(CO)_4(RCO)Mn(SiR'_3)$, resulting from hydrogen atom abstraction from the silane oxidative-addition product $(CO)_4(RCO)Mn(H)(SiR'_3)$, associates $FpCOCH_3$. The resulting 19-electron adduct, perhaps having its odd electron partially delocalized on the ligated $FpCOCH_3$, could rearrange to a 17-electron manganese system $(CO)_4(RCO)MnCH(OSiR'_3)Fp$ that shares a μ-siloxyalkylidene ligand with a Fp moiety. Subsequent hydrogen atom transfer to the manganese center and reductive elimination of $FpCH(OSiR'_3)R$ product would regenerate the active catalyst, $(CO)_4MnCOR$.

Acid-Catalyzed Isomerization and Deuterium Exchange of Rhenium Alkene Complexes via In-Place Rotation of an Agostic Alkylrhenium Cation

Charles P. Casey* and Chae S. Yi

Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706

Received August 2, 1990

Summary: $C_5H_5(CO)_2Re(cis\text{-}CH_3CH{=}CHCH_3)$ (**1**) isomerized to a 45:55 equilibrium mixture of **1** and $C_5H_5(CO)_2Re(trans\text{-}CH_3CH{=}CHCH_3)$ (**2**) upon treatment with CF_3CO_2H in CH_2Cl_2. In the isomerization of **1** by CF_3CO_2D, the initially formed **2** was monodeuterated at the vinyl position. Treatment of $C_5H_5(CO)_2Re(CH_2{=}CHCH_2CH_3)$ (**3**) with CF_3CO_2D led only to deuterium exchange of the vinyl hydrogens; no formation of **1** or **2** was observed. These data are consistent with a mechanism involving agostic rhenium alkyl complexes that undergo "in-place rotation" and deprotonation much more rapidly than formation of a free alkylrhenium intermediate.

We have recently devised several new syntheses of $C_5H_5(CO)_2Re(alkene)$ complexes from reactions of alkynes with the heterobimetallic dihydride $C_5H_5(CO)_2(H)RePt(H)(PPh_3)_2$,[1] from rearrangement of rhenium carbene complexes,[2] and from reaction of $C_5H_5(CO)_2ReH^-$ with allyl halides[3] that complement previous syntheses from $C_5H_5(CO)_2Re(THF)$ and alkenes.[4] We have begun to explore the reactivity of these rhenium alkene complexes and have found that reaction with $(C_6H_5)_3C^+$ leads to hydride abstraction and formation of (π-allyl)rhenium cations.[5]

---

[1] Casey, C. P.; Rutter, E. W., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 8917.

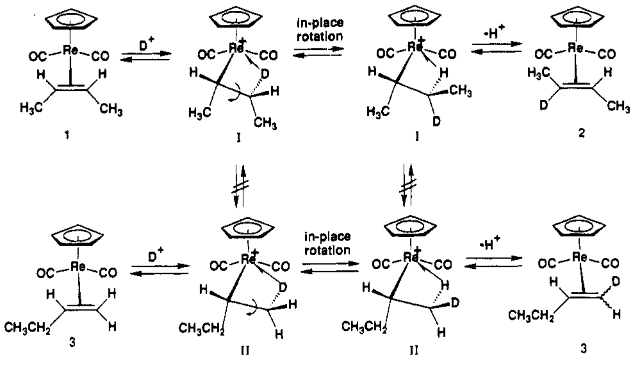
[2] Casey, C. P.; Vosejpka, P. C.; Askham, F. R. *J. Am. Chem. Soc.* **1990**, *112*, 3713.

[3] Casey, C. P.; Yi, C. S. Unpublished results.

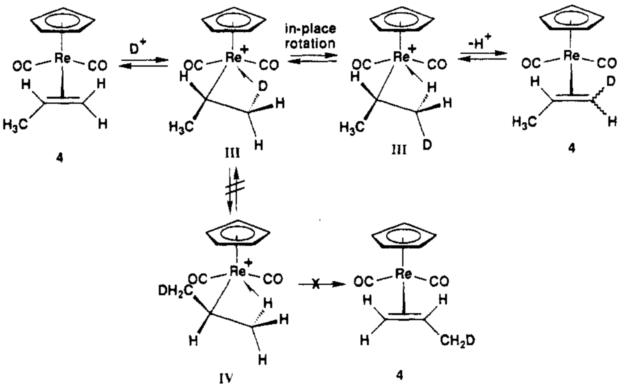
[4] (a) Sellmann, D.; Kleinschmidt, E. *Z. Naturforsch., B* **1977**, *32B*, 795. (b) Einstein, F. W. B.; Jones, R. H.; Klahn-Oliva, A. H.; Sutton, D. *Organometallics* **1986**, *5*, 2476. (c) Caulton, K. G. *Coord. Chem. Rev.* **1981**, *38*, 1.

0276-7333/91/2310-0033$02.50/0

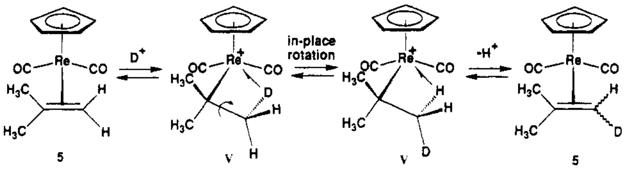
Scheme I



Scheme II



Scheme III



Because considerable attention has been focused on the role of protonation of transition-metal alkene complexes in alkene polymerization,[6] we initiated a study of the reaction of rhenium alkene complexes with protic acids. Here we report that rhenium alkene complexes undergo acid-catalyzed cis–trans isomerization initiated by protonation. Evidence will be presented that supports a mechanism involving agostic alkylrhenium intermediates that undergo "in-place rotation" and deprotonation thousands of times faster than breaking of the agostic interaction.

Isomerization of the *cis*-2-butene complex $C_5H_5(CO)_2Re(cis\text{-}CH_3CH{=}CHCH_3)$ (**1**)[1] to a 45:55 equilibrium mixture of **1** and the *trans*-2-butene complex $C_5H_5(CO)_2Re(trans\text{-}CH_3CH{=}CHCH_3)$ (**2**)[7] occurred within 30 min at room temperature upon treatment with excess CF_3CO_2H (1.40 M) in CH_2Cl_2.[8] ^1H NMR spectroscopy indicated that none of the 1-butene complex $C_5H_5(CO)_2Re(CH_2{=}CHCH_2CH_3)$ (**3**) was formed (Scheme I). When the isomerization of **1** catalyzed by CF_3CO_2D (1.37 M) was monitored by ^1H NMR spectroscopy at low conversion, the initially formed *trans*-2-butene complex **2** was monodeuterated at the vinyl position. After prolonged treatment with CF_3CO_2D, the vinyl positions of both **1** and **2** were extensively deuterated but no deuteration of the methyl groups was seen by ^1H NMR spectroscopy. These results are readily explained by stereospecific protonation of a vinyl carbon, rotation about the former double bond, and stereospecific deprotonation. It seemed curious that the postulated (2-butyl)rhenium intermediate I did not deprotonate to give 1-butene complex **3**.

Treatment of 1-butene complex **3** with excess CF_3CO_2H did not lead to formation of 2-butene complexes **1** and **2**. To determine whether **3** was being protonated under these conditions, reaction of **3** with CF_3CO_2D (1.28 M) in CD_2Cl_2 was followed by ^1H and ^2H NMR spectroscopy. Exchange of deuterium into the terminal vinyl position occurred most rapidly, exchange into the secondary vinyl position occurred about 5 times more slowly, and no exchange into the ethyl group was observed.[9]

The rapid exchange into the terminal vinyl position of **3** requires the (2-butyl)rhenium intermediate II, but this must be different from the (2-butyl)rhenium intermediate I involved in *cis*-2-butene isomerization and exchange reactions, since no interconversion between 1-butene and 2-butene complexes was observed. To explain these observations, we propose that the two intermediates fail to interconvert because of an unusually strong agostic interaction involving a cationic third-row transition metal. Cis–trans isomerization and deuterium exchange can be explained by what has been termed an "in-place rotation" of an agostic alkyl group.[6c,10]

For the neutral complex $Cp_2Nb(CH_2{=}CHCH_3)H$, Green and Bercaw[10] found that exchange of Nb–H with the terminal methylene group was 3 times faster than exchange with the methyl group. For the cationic complex $Cp_2W(CH_2{=}CHCH_3)H^+$, Cooper[6c] found a ~20 times faster exchange of the tungsten hydride with the terminal methylene group than with the methyl group. In both cases, the rate differences were explained in terms of in-place rotation of an agostic alkylmetal complex.

To get a more quantitative measure of the strength of the agostic interaction, we studied the deuteration of the propene complex $C_5H_5(CO)_2Re(CH_2{=}CHCH_3)$ (**4**)[1] with excess CF_3CO_2D (0.69 M) in CD_2Cl_2 (Scheme II). In-

---

[5] Casey, C. P.; Yi, C. S. *Organometallics* **1990**, *9*, 2413.

[6] (a) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1. (b) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. (c) McNally, J. P.; Cooper, N. J. *Organometallics* **1988**, *7*, 1704. (d) Brookhart, M.; Lincoln, D. M.; Volpe, A. F., Jr.; Schmidt, G. F. *Organometallics* **1989**, *8*, 1212. (e) Doherty, N. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 2670. (f) Jordan, R. F.; Bradly, P. K.; Baenziger, N. C.; LaPointe, R. E. *J. Am. Chem. Soc.* **1990**, *112*, 1289.

[7] $C_5H_5(CO)_2Re(trans\text{-}CH_3CH{=}CHCH_3)$ (**2**): ^1H NMR (CD_2Cl_2, 200 MHz) δ 5.24 (s, C_5H_5), 3.0 (m, CH), 1.8 (m, CH_3); ^{13}C NMR (CD_2Cl_2, 126 MHz) δ 206.0 (s, CO), 202.3 (s, CO), 86.4 (d, J = 179.1 Hz, C_5H_5), 43.8 (d, J = 153.3 Hz, CH), 25.8 (q, J = 126.6 Hz, CH_3); IR (CH_2Cl_2) 1955 (s), 1876 (s) cm^{-1}; HRMS calcd for $C_{11}H_{13}O_2Re$ 364.0474, found 364.0472. Anal. Calcd for $C_{11}H_{13}O_2Re$: C, 36.35; H, 3.61. Found: C, 36.15; H, 3.50. $C_5H_5(CO)_2Re(CH_2{=}CHCH_2CH_3)$ (**3**): ^1H NMR ($CDCl_3$, 200 MHz) δ 5.18 (s, C_5H_5), 3.00 (dddd, J = 11.5, 8.0, 8.0, 5.0 Hz, $CH_2{=}C\mathit{H}$), 2.35 (dd, J = 8.0, 2.0 Hz, $C\mathit{H}H{=}CH$), 2.0 (dqd, J = 15.0, 8.0, 5,0 Hz, $C\mathit{H}HCH_3$), 1.95 (dd, J = 11.5, 2.0 Hz, $CH\mathit{H}{=}CH$), 1.45 (dqd, J = 15.0, 8.0, 8.0 Hz, $C\mathit{H}HCH_3$), 1.05 (t, J = 8.0 Hz, CH_3); ^{13}C NMR (CD_2Cl_2, 126 MHz) δ 204.7 (s, CO), 203.8 (s, CO), 86.2 (d, J = 179.4 Hz, C_5H_5), 43.0 (d, J = 152.9 Hz, $CH_2{=}\mathit{C}H$), 32.5 (t, J = 127.6 Hz, $\mathit{C}H_2{=}CH$), 19.7 (t, J = 127.5 Hz, $\mathit{C}H_2CH_3$), 19.0 (q, J = 121.8 Hz, $CH_2\mathit{C}H_3$); IR (hexane) 1973 (s), 1903 (s) cm^{-1}; HRMS calcd for $C_{11}H_{13}O_2Re$ 364.0474, found 364.0474. $C_5H_5(CO)_2Re(CH_2{=}C(CH_3)_2)$ (**5**): ^1H NMR (CD_2Cl_2, 200 MHz) δ 5.25 (s, C_5H_5), 2.43 (s, $CH_2{=}$), 1.88 (s, CH_3); ^{13}C NMR (CD_2Cl_2, 126 MHz) δ 204.2 (s, CO), 86.5 (d, J = 172.5 Hz, C_5H_5), 59.9 (s, $CH_2{=}\mathit{C}$), 31.7 (q, J = 126.3 Hz, CH_3), 25.8 (t, J = 155.9 Hz, $\mathit{C}H_2{=}C$); IR (hexane) 1969 (s), 1901 (s) cm^{-1}; HRMS calcd for $C_{11}H_{13}O_2Re$ 364.0474, obsd 364.0465. Anal. Calcd for $C_{11}H_{13}O_2Re$: C, 36.35; H, 3.61. Found: C, 35.94; H, 3.26.

[8] $HBF_4 \cdot OEt_2$ in CH_2Cl_2 also catalyzed the isomerization of **1**. Under similar conditions, CF_3CO_2H-catalyzed isomerization of **1** was about 10 times slower in benzene or toluene than in CH_2Cl_2.

[9] From both ^1H NMR and ^2H NMR spectroscopy, no deuterium incorporation into the ethyl group was seen and 5% deuterium incorporation would have been easily detected by ^2H NMR spectroscopy.

[10] Bercaw, J. E.; Burger, B. J.; Green, M. L. H.; Santarsiero, B. D.; Sella, A.; Trimmer, M. S.; Wong, L.-L. *J. Chem. Soc., Chem. Commun.* **1989**, 734.

corporation of deuterium was followed by ^1H and ^2H NMR spectroscopy. Exchange of deuterium into the terminal vinyl position was about half-complete after 10 min at room temperature, and exchange into the secondary vinyl position was about 10 times slower. After 27 days, ^2H NMR spectroscopy showed that all of the vinyl positions of **4** were fully deuterated but the methyl group of **4** had less than 5% deuterium. This indicates that the agostic intermediate III must undergo in-place rotation and deprotonation several thousand times faster than the agostic interaction is broken.

The possibility that the agostic intermediate III might be significantly more stable than its diastereomer IV and thus inhibit exchange into the methyl group was tested by examining deuterium incorporation into the 2-methylpropene complex $C_5H_5(CO)_2Re(CH_2{=}CMe_2)$ (**5**)[7] since its agostic intermediate V is symmetric (Scheme III). The exchange rate of deuterium into **5** with CF_3CO_2D was approximately the same as that as into **3**, but deuterium was found only in the vinyl position of **5** and not in the methyl groups.

Acknowledgment. Financial support from the National Science Foundation is gratefully acknowledged. C.P.C. thanks the Alexander von Humboldt Stiftung for a senior award.

Unsaturation in a High-Nuclearity Metal Carbonyl Cluster Complex. Synthesis, Structures, and Interconversions of $Pt_2Os_4(CO)_{12}(COD)_2$ and $Pt_2Os_4(CO)_{11}(COD)_2$

Richard D. Adams* and Wengan Wu

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

Received September 27, 1990

Summary: The two new platinum-osmium carbonyl cluster complexes $Pt_2Os_4(CO)_{12}(COD)_2$ (**1**) and $Pt_2Os_4(CO)_{11}(COD)_2$ (**2**) were obtained from the reaction of $Pt_2Os_4(CO)_{18}$ with 1,5-cyclooctadiene (COD) at 97 °C. Both compounds consist of a bicapped Os_4 tetrahedron. Compound **1** is coordinatively saturated, while compound **2** is coordinatively unsaturated. The latter contains several unusually short metal-metal bonds and readily adds CO to give **1** in good yield.

An important feature of coordinatively unsaturated complexes is their ability to add new ligands under mild conditions.[1] Although there are relatively few examples of coordinatively unsaturated cluster complexes,[2] this feature may play a key role in the future development of these compounds as catalysts.[3] We now wish to report a new example of coordination unsaturation in a high-nuclearity metal carbonyl cluster complex and the observation that the complex can add and eliminate CO without the formal cleavage of a metal-metal bond.

From the reaction of $Pt_2Os_4(CO)_{18}$[4] with 1,5-cyclooctadiene (COD) in refluxing heptane solvent we have isolated the two new complexes $Pt_2Os_4(CO)_{12}(COD)_2$ (**1**; 55% yield) and $Pt_2Os_4(CO)_{11}(COD)_2$ (**2**; 9% yield).[5] The structures of both complexes have been determined by single-crystal X-ray diffraction methods, and ORTEP drawings of their molecular structures are shown in Figure

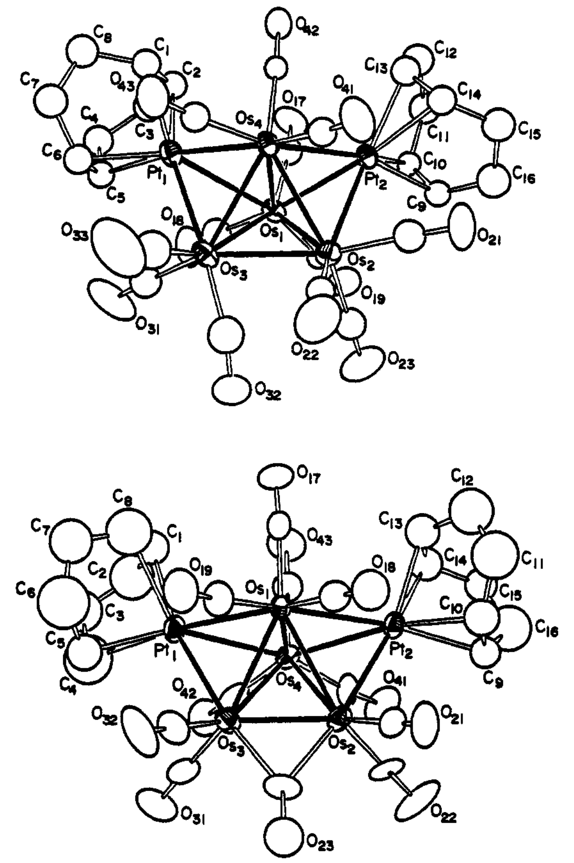


Figure 1. ORTEP diagrams of $Pt_2Os_4(CO)_{12}(COD)_2$ (**1**; top) and $Pt_2Os_4(CO)_{11}(COD)_2$ (**2**; bottom) showing 50% probability thermal ellipsoids. Selected bond distances (Å) for **1** [**2**] are as follows: Os(1)–Os(2) = 2.859 (1) [2.835 (1)], Os(1)–Os(3) = 2.759 (1) [2.834 (1)], Os(1)–Os(4) = 2.832 (1) [2.705 (1)], Os(1)–Pt(1) = 2.975 (1) [2.857 (1)], Os(1)–Pt(2) = 2.737 (1) [2.883 (1)], Os(2)–Os(3) = 2.786 (1) [2.530 (1)], Os(2)–Os(4) = 2.785 (1) [2.831 (1)], Os(2)–Pt(2) = 2.855 (1) [2.614 (1)], Os(3)–Os(4) = 2.868 (1) [2.838 (1)], Os(3)–Pt(1) = 2.741 (1) [2.609 (1)], Os(4)–Pt(1) = 2.711 (1) [2.865 (1)], Os(4)–Pt(2) = 2.784 (1) [2.840 (1)].

---

[1] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 241.

[2] (a) Adams, R. D.; Horvath, I. T. *Prog. Inorg. Chem.* **1985**, *33*, 127. (b) Mingos, D. M. P.; May, A. In *Chemistry of Metal Clusters*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH: New York, 1990; Chapter 2.

[3] (a) Muetterties, E. L.; Krause, M. J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 135. (b) Muetterties, E. L. *Catal. Rev.—Sci. Eng.* **1981**, *23*, 69. (c) Süss-Fink, G.; Neumann, In *Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Ed.; Wiley: New York, 1989; Vol. 5, Chapter 7, p 231.

[4] Sundberg, P. *J. Chem. Soc., Chem. Commun.* **1987**, 1307.

[5] A 36-mg amount of $Pt_2Os_4(CO)_{18}$ was allowed to react with 0.36 mL of COD in heptane solvent at 97 °C for 4.5 h. The products were isolated by TLC on silica gel. The first band yielded 20.5 mg of red-brown **1** (55%), and the second band yielded 3.6 mg of yellow-brown **2** (9%). IR for **1** (ν_{CO}, cm^{-1}; in hexane): 2059 (m), 2022 (w), 2005 (vs), 1955 (w), 1944 (w). IR for **2** (ν_{CO}, cm^{-1}; in CH_2Cl_2): 2014 (vs), 1991 (vs), 1982 (sh), 1952 (w), 1926 (vw), 1844 (vw, br). ^1H NMR for **1** (δ; in $CDCl_3$): 5.69 (t, 8 H, $^2J_{Pt-H}$ = 61.5 Hz), 2.36 (m, 8 H), 1.92 (m, 8 H). ^1H NMR for **2** (δ; in C_6D_6): 5.03 (s, br, 4 H), 4.33 (s, br, 4 H), 1.36 (s, br, 8 H), 0.71 (s, br, 8 H).

0276-7333/91/2310-0035$02.50/0