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Communications

Ruthenium Cluster Mediated Transformation of Linear Alkenes into Trienyl Ligands. Activation of Five $C(sp^3)-H$ Bonds of 1-Octene, 1-Nonene, and 1-Decene

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Summary: The treatment of $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-ampy})(CO)_{16}]$ *(*H_2*ampy = 2-amino-6-methylpyridine) with 1-octene, 1-nonene, and 1-decene affords heptanuclear derivatives containing trienyl ligands that arise from the unusual activation of five* $C(sp^3)-H$ *bonds of linear alkenes.*

In the last three decades, the activation of C−H bonds promoted by transition-metal complexes has been a major research theme in organometallic chemistry and a plethora of reports on this field have been published.[1] Currently, the primary objective of this research activity is the use of these processes in chemoselective organic synthesis. However, the search for new processes and the understanding of the factors that control these reactions are also highly active research fields.[1]

In this context, $C(sp^3)-H$ bonds are generally quite stable and difficult to cleave. In fact, the known examples of $C(sp^3)-H$ bond activation by oxidative addition processes are fewer than those known for $C(sp^2)-H$ bonds, and even smaller is the number of known homogeneous processes by which various $C(sp^3)-H$ bonds of the same molecule are cleaved.[1] Although significant contributions on dehydrogenation of acyclic alkanes under homogeneous conditions have been published,[1−3] these reports do not generally describe the formation of polyenes or complexes containing polyene or polyenyl ligands as reaction products. Remarkable exceptions are a couple of reports that describe the dehydrogenation of linear alkanes to dienes[3] and the conversion of hexane to a complex mixture that includes hexatriene and benzene.[2b] The latter process, in which benzene is presumably formed via hexatriene, represents a total loss of eight hydrogen atoms. Multiple dehydrogenation of cyclic alkanes and some alkenes containing five-[1,4,5] and six-membered[1,5,6] rings has been reported. In these cases, their aromatization leads to η^5-cyclopentadienyl and η^6-arene derivatives of considerable stability.

We now report the synthesis and characterization of some heptaruthenium cluster complexes containing trienyl ligands that arise from the cleavage of five $C(sp^3)-H$ bonds of linear 1-alkenes.

Two isomeric octatrienyl derivatives were synthesized by heating to reflux temperature a solution of the basal edge-bridged square-pyramidal hexaruthenium cluster $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-}CO)_2(CO)_{14}]$[7] (**1**; H_2ampy = 2-amino-6-methylpyridine) in 1-octene. Both compounds were separated by preparative TLC and were subsequently identified as the heptanuclear complexes $[Ru_7(\mu_3\text{-}H)(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-}\eta^3\text{:}\eta^4\text{-}MeC_7H_8)(\mu\text{-}CO)_3(CO)_{12}]$ (**2a**) and $[Ru_7(\mu_3\text{-}H)(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-}\eta^3\text{:}\eta^4\text{-}C_7H_8Me)(\mu\text{-}CO)_3(CO)_{12}]$ (**2b**) (Scheme 1). The related trienyl derivatives $[Ru_7(\mu_3\text{-}H)(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-}\eta^3\text{:}\eta^4\text{-}MeC_7H_7Me)(\mu\text{-}CO)_3(CO)_{12}]$ (**3a**), $[Ru_7(\mu_3\text{-}H)(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-}\eta^3\text{:}\eta^4\text{-}EtC_7H_8)(\mu\text{-}CO)_3(CO)_{12}]$ (**3b**), $[Ru_7(\mu_3\text{-}H)(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-}\eta^3\text{:}\eta^4\text{-}C_7H_8Et)(\mu\text{-}CO)_3(CO)_{12}]$ (**3c**), $[Ru_7(\mu_3\text{-}H)(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-}\eta^3\text{:}\eta^4\text{-}MeC_7H_7Et)(\mu\text{-}CO)_3(CO)_{12}]$ (**4a**),

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[1] For selected reviews on C−H bond activation, see: (a) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507. (b) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154. (c) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879. (d) Jones, W. D. In *Topics in Organometallic Chemistry: Activation of Unreactive Bonds and Organic Cemistry*; Murai, S., Ed.; Springer: Heidelberg, Germany, 1999; p 9. (e) Dyker, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 1699. (f) Guari, Y.; Sabo-Etienne, S.; Chaudret, B. *Eur. J. Inorg. Chem.* **1999**, 1047. (g) Jun, C.-H.; Moon, C. W.; Lee, D.-Y. *Chem. Eur. J.* **2002**, *8*, 2423. (h) Jia, C.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633. (i) Shilov, A. E.; Shul'pin, G. B. In *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*; Kluwer: Dordrecht, The Netherlands, 2000. (j) Sen, A. *Acc. Chem. Res.* **1998**, *31*, 550. (k) Kakiuchi, F.; Murai, S. In *Topics in Organometallic Chemistry: Activation of Unreactive Bonds and Organic Synthesis*; Murai, S., Ed.; Springer: Heidelberg, Germany, 1999; p 47. (l) Crabtree, R. H. *Dalton Trans.* **2001**, 2437. (m) Kakiuchi, F.; Chatani, N. *Adv. Synth. Catal.* **2003**, *345*, 1077.

[2] For recent examples of alkane dehydrogenation, see: (a) Rodríguez, P.; Díaz-Requejo, M. M.; Belderraín, T. R.; Trofimenko, S.; Nicasio, M. C.; Pérez, P. J. *Organometallics* **2004**, *23*, 2162. (b) Zhu, K.; Achord, P. D.; Zhang, X.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2004**, *126*, 13044. (c) Felk, U.; Kaminsky, W.; Goldberg, K. I. *J. Am. Chem. Soc.* **2003**, *125*, 15286. (d) Hall, M. B.; Fan, H.-J. *Adv. Inorg. Chem.* **2003**, *54*, 321.

[3] (a) Baudry, D.; Ephritikhine, M.; Felkin, H.; Zakrzewski, J. *J. Chem. Soc., Chem. Commun.* **1982**, 1235. (b) Baudry, D.; Ephritikhine, M.; Felkin, H.; Zakrzewski, J. *Tetrahedron Lett.* **1984**, 1283.

[4] (a) Crabtree, R. H.; Mihelcic, J. M.; Quirck, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 7738. (b) Schnabel, R. C.; Roddick, D. M. *Organometallics* **1996**, *15*, 3550.

[5] Koola, J. D.; Roddick, D. M. *J. Am. Chem. Soc.* **1991**, *113*, 1450.

[6] (a) Gupta, M.; Hagen, C.; Flesher, R. J.; Kaska, W. C.; Jensen, C. M. *J. Chem. Soc., Chem. Commun.* **1997**, 461. (b) Gupta, M.; Hagen, C.; Kaska, W. C.; Cramer, R. E.; Jensen, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 840. (c) Nizova, G. V.; Chaudret, B.; He, X.-D.; Shul'pin, G. B. *Bull. Russ. Acad. Sci.* **1992**, *41*, 1138. (d) Hodges, R. J.; Garnett, J. L. *J. Phys. Chem.* **1968**, *72*, 1673. (e) Crabtree, R. H.; Parnell, C. P.; Uriarte, R. J. *Organometallics* **1987**, *6*, 696.

[7] (a) Cabeza, J. A.; del Río, I.; García-Álvarez, P.; Riera, V.; Suárez, M.; García-Granda, S. *Dalton Trans.* **2003**, 2808. (b) Cabeza, J. A.; del Río, I.; García-Álvarez, P.; Miguel, D.; Riera, V. *Inorg. Chem.* **2004**, *43*, 5450.

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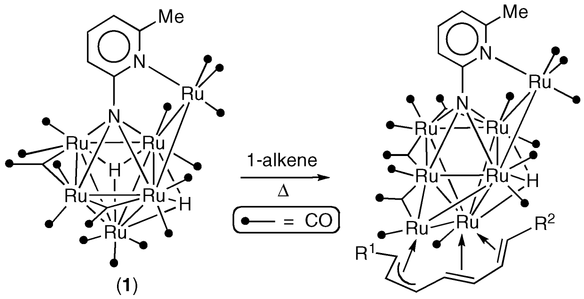
Scheme 1



(**1**)

1-alkene	T (°C)	t (h)	products	yield (%)
1-octene	123	8	**2a**: R^1 = Me; R^2 = H	22
			2b: R^1 = H; R^2 = Me	8
1-nonene	146	4	**3a**: R^1 = R^2 = Me	38
			3b: R^1 = Et; R^2 = H	8
			3c: R^1 = H; R^2 = Et	6
1-decene	168	2	**4a**: R^1 = Me; R^2 = Et	25
			4b: R^1 = Et; R^2 = Me	25

and $[Ru_7(\mu_3\text{-}H)(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-}\eta^3{:}\eta^4\text{-}EtC_7H_7Me)(\mu\text{-}CO)_3(CO)_{12}]$ (**4b**) were obtained from similar reactions using 1-nonene (**3a**−**c**) or 1-decene (**4a**,**b**) as solvents (Scheme 1). Compounds **4a** and **4b** could not be separated by TLC. In all cases, heating was maintained until the consumption of the starting material **1** was observed (IR monitoring). As shown in Scheme 1, the reaction time is strongly influenced by the reaction temperature (the solvent boiling point). A black insoluble residue, arising from the thermal decomposition of part of the starting material,[8,9] was also formed in all occasions. This decomposition provides the $Ru(CO)_n$ fragments necessary to obtain heptanuclear products from a hexanuclear precursor.

The structures of compounds **2a**,**b** and **3a**−**c** were determined by X-ray diffraction.[10] All structures are very similar, differing only in the nature of the R^1 and R^2 groups attached to the ends of the trienyl fragment of each compound. As a representative example, the molecular structure of **3a** is shown in Figure 1. These structures are comparable to that of $[Ru_7(\mu_3\text{-}H)(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-}\eta^5{:}\eta^6\text{-ind})(\mu\text{-}CO)_3(CO)_{11}]$ (ind = indenyl),[9] which has an analogous $Ru_7(\mu_3\text{-}H)(\mu_5\text{-}\kappa^2\text{-ampy})$ fragment and an indenyl ligand coordinated to the same ruthenium atoms as the trienyl ligands of **2**−**4**. These ligands span the Ru(6) and Ru(7) atoms in such a way that they are attached to Ru(6) through four carbon atoms (as an η^4-butadiene fragment) and to Ru(7) through three carbon atoms (as an η^3-allyl fragment). All the trienyl ligands have the same stereochemistry, with the R^1 (≠H) and the diene substituents of the allyl group being in syn and anti positions, respectively, and the allyl and R^2 (≠H) substituents of the diene group in trans arrangements (Scheme 1, Figure 1).

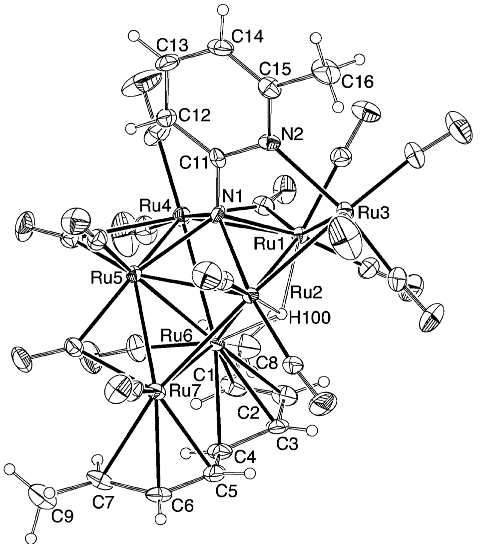


Figure 1. Molecular structure of compound **3a**. Selected bond distances (Å): C(1)−C(2) = 1.398(13), C(1)−C(8) = 1.513(13), C(2)−C(3) = 1.400(12), C(3)−C(4) = 1.430(11), C(4)−C(5) = 1.429(12), C(5)−C(6) = 1.411(12), C(6)−C(7) = 1.414(12), C(7)−C(9) = 1.491(13), C(1)−Ru(6) = 2.338(8), C(2)−Ru(6) = 2.259(8), C(3)−Ru(6) = 2.247(7), C(4)−Ru(6) = 2.390(7), C(5)−Ru(7) = 2.223(7), C(6)−Ru(7) = 2.222(7), C(7)−Ru(7) = 2.307(7).

As stated above, compounds **4a**,**b** could not be separated. However, their structures could be ascertained (Scheme 1) by analyzing the ^1H NMR spectrum of the mixture (see the Supporting Information), which contains six resonances assignable to methyl groups: two singlets (methyls of ampy ligands), two doublets (methyls attached to CH groups), and two triplets (methyls attached to CH_2 groups). Hypothetical isomers having one terminal propyl group on the trienyl ligand would not show methyls as doublets. In addition, most features of the IR and ^1H NMR spectra of the mixture of **4a**,**b** are very similar to those of complexes **2** and **3**,[11] as expected for compounds having closely related structures.

Taking into account that the reagents used are terminal alkenes and that the major products of the reactions with 1-nonene and 1-decene have internal trienyl ligands (R^1, R^2 ≠ H in Scheme 1), their synthesis (and probably the synthesis of the minor products as well) should involve not only the removal of five hydrogen atoms from the original alkene but also the exchange of at least one hydrogen atom between carbon atoms of the hydrocarbon chain. The high temperatures required by these processes and the relative abundance of the products of each reaction indicate that the compounds having internal trienyl ligands (such as **3a**) are thermodynamically more stable than those having terminal trienyl ligands (such as **3b**,**c**).

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[8] Cabeza, J. A.; del Río, I.; García-Álvarez, P.; Miguel, D. *Organometallics* **2006**, *25*, 5672.

[9] Cabeza, J. A.; del Río, I.; Fernández-Colinas, J. M.; García-Álvarez, P.; Miguel, D. *Organometallics* **2007**, *26*, 1414.

[10] Selected crystallographic data are as follows. $(\mathbf{2a})_2\cdot 0.25CH_2Cl_2\cdot CHCl_3$: $C_{59.25}H_{37.5}Cl_{3.5}N_4O_{30}Ru_{14}$, $M_r = 2824.49$, triclinic, space group $P1$, $Z = 2$, $a = 11.949(2)$ Å, $b = 17.876(4)$ Å, $c = 18.820(4)$ Å, $\alpha = 88.188(4)°$, $\beta = 80.155(3)°$, $\gamma = 85.921(3)°$, $U = 3950(1)$ Å^3, $T = 296(2)$ K, μ(Mo Kα) = 2.790 mm^{-1}, wR1(F^2) = 0.0458 ($I > 2\sigma(I)$), CCDC 635238. $\mathbf{2b}\cdot 0.5C_2H_4Cl_2$: $C_{30}H_{20}ClN_2O_{15}Ru_7$, $M_r = 1391.42$, monoclinic, space group $C2/c$, $Z = 8$, $a = 33.809(7)$ Å, $b = 11.917(2)$ Å, $c = 18.550(4)$ Å, $\beta = 93.714(4)$, $U = 7458(3)$ Å^3, $T = 296(2)$ K, μ(Mo Kα) = 2.901 mm^{-1}, wR1(F^2) = 0.0749 ($I > 2\sigma(I)$), CCDC 635239. $\mathbf{3a}\cdot 0.5C_2H_4Cl_2$: $C_{31}H_{22}ClN_2O_{15}Ru_7$, $M_r = 1405.45$, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 10.094(3)$ Å, $b = 10.685(3)$ Å, $c = 19.963(6)$ Å, $\alpha = 96.418(6)°$, $\beta = 102.817(6)°$, $\gamma = 109.754(5)°$, $U = 1935\ (1)$ Å^3, $T = 296(2)$ K, μ(Mo Kα) = 2.797 mm^{-1}, wR1(F^2) = 0.0347 ($I > 2\sigma(I)$), CCDC 635240. $\mathbf{3b}\cdot 0.5C_2H_4Cl_2$: $C_{31}H_{22}ClN_2O_{15}Ru_7$, $M_r = 1405.45$, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 10.015(5)$ Å, $b = 10.370(5)$ Å, $c = 20.547(11)$ Å, $\alpha = 93.227(10)°$, $\beta = 102.798(10)°$, $\gamma = 109.058(9)°$, $U = 1948(2)$ Å^3, $T = 296(2)$ K, μ(Mo Kα) = 2.778 mm^{-1}, wR1(F^2) = 0.0649 ($I > 2\sigma(I)$), CCDC 635241. $\mathbf{3c}\cdot C_5H_{12}$: $C_{35}H_{32}N_2O_{15}Ru_7$, $M_r = 1428.12$, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 10.678(12)$ Å, $b = 29.84(3)$ Å, $c = 14.767(16)$ Å, $\beta = 109.14(2)°$, $U = 4445(8)$ Å^3, $T = 296(2)$ K, μ(Mo Kα) = 2.379 mm^{-1}, wR1(F^2) = 0.0745 ($I > 2\sigma(I)$), CCDC 635242.

[11] Selected IR data (CH_2Cl_2, cm^{-1}; ν_{CO}): 2068 (m), 2033 (s), 2015 (vs), 2005 (s, sh), 1974 (m, br), 1934 (w, br), 1825 (w, br) (**2a**); 2069 (m), 2033 (s), 2014 (vs), 2004 (s, sh), 1974 (m, br), 1933 (w, br), 1825 (w, br) (**2b**); 2068 (m), 2033 (s), 2015 (vs), 2005 (s, sh), 1974 (m, br), 1934 (w, br), 1825 (w, br) (**3a**); 2068 (m), 2033 (s), 2015 (vs), 2005 (s, sh), 1974 (m, br), 1934 (w, br), 1825 (w, br) (**3b**); 2068 (m), 2033 (s), 2013 (vs), 2002 (s, sh), 1974 (m, br), 1934 (w, br), 1825 (w, br) (**3c**); 2068 (m), 2032 (s), 2013 (vs), 2002 (s, sh), 1973 (m, br), 1932 (w, br), 1825 (w, br) (**4a** + **4b**). Selected ^1H NMR data (300 MHz, 293 K, $CDCl_3$; $\delta(\mu_3\text{-}H)$): −18.54 (s) (**2a**); −17.82 (s) (**2b**); −17.93 (s) (**3a**); −18.53 (s) (**3b**); −17.86 (s) (**3c**); −17.92 (s) and −17.96 (s) (**4a** + **4b**).

Unfortunately, the reactions are not catalytic. GC analyses of the solvents of the reaction mixtures did not show polydehydrogenated hydrocarbons. Most probably, simple alkenes are unable to replace polyalkenes and polyalkenyl ligands from the metal clusters that contain them.

A few examples of metal cluster promoted dehydrogenation of linear alkenes have been previously published. The reactions of *trans*-2-heptene and 2,4-heptadiene with the hexanuclear cluster $[Ru_6(\mu_4\text{-}S)(\mu\text{-}CO)_3(CO)_{15}]$ give the dienyl derivative $[Ru_6(\mu_3\text{-}H)(\mu_4\text{-}S)(\mu\text{-}\eta^2{:}\eta^3\text{-}MeC_5H_5Me)(CO)_{15}]$.[12] *cis*-2-Butene reacts with $[Ru_3(CO)_{12}]$ to give the dimetalated allyl derivative $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^3\text{-}MeC_3H_2)(CO)_9]$.[13] The mononuclear allyl complexes $[RuH(\eta^3\text{-}RC_3H_4)(CO)_3]$ (R = H, Et) have been prepared from $[Ru_3(CO)_{12}]$ and 1-propene or 1-pentene.[14] The reaction of $[Ru_3(CO)_{12}]$ with 1-pentene also gives the penta-1,3-diene derivative $[Ru(\eta^4\text{-}MeC_4H_5)(CO)_3]$. It should be noted that these metal cluster promoted dehydrogenations of linear alkenes involve the activation of no more than three $C(sp^3)-H$ bonds and that, in some cases, they are accompanied by metal cluster fragmentation.

The tetranuclear cluster $[Ru_4(\mu_3\text{-}\eta^4\text{-}C_5H_6)(\mu_4\text{-}\eta^7\text{-}C_{10}H_{12})(CO)_8]$ is the only previously known metal cluster containing a trienyl ligand related to those of compounds **2**−**4**. However, the trienyl ligand of this cluster arises from the coupling of two pent-1-en-3-yne molecules.[15]

The results described in this communication, coupled with the previously known data on metal complex promoted dehydrogenation of linear alkenes, allow us to conclude that to achieve extensive dehydrogenation reactions (a) it is important to carry out the reactions at high temperatures (>120 °C), (b) it is important to use metal cluster complexes as precursors, so that they allow the coordination of many unsaturated CC bonds, and (c) the clusters, precursors, and products should be thermally robust to prevent extensive decomposition at the working temperatures. This can only be achieved with clusters containing bridging ligands, such as the ampy ligand used in this work.[8,9,16]

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Supporting Information Available: Text giving synthetic, spectroscopic, and analytical details for all isolated compounds and CIF files giving crystallographic data for the compounds studied by X-ray diffraction. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Adams, R. D.; Babin, J. E.; Tasi, M.; Wolfe, T. A. *J. Am. Chem. Soc.* **1988**, *110*, 7073.

(13) Rao, K. M.; Angelici, R. J.; Young, V. G. *Inorg. Chim. Acta* **1992**, *198*, 211.

(14) Wuu, Y. M.; Bentsen, J. G.; Brinkley, C. G.; Wrighton, M. S. *Inorg. Chem.* **1987**, *26*, 530.

(15) Zuno-Cruz, F. J.; Sánchez-Cabrera, G.; Rosales-Hoz; M. J.; Nöth, H. *J. Organomet. Chem.* **2002**, *649*, 43.

(16) (a) Cabeza, J. A.; del Río, I.; García-Álvarez, P.; Miguel, D. *Can. J. Chem.* **2006**, *84*, 105. (b) Cabeza, J. A.; del Río, I.; García-Álvarez, P.; Miguel, D. *Inorg. Chem.* **2006**, *45*, 6020.