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# Sequential Electrophile/Nucleophile Additions for $\eta^2$-Cyclopentadiene Complexes of Osmium(II), Ruthenium(II), and Rhenium(I)

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*Summary: A series of $d^6$ transition-metal complexes of the type $ML_5(\eta^2\text{-CpH})$, where $ML_5 = [Os^{II}(NH_3)_5]^{2+}$, $[Ru^{II}(NH_3)_5]^{2+}$, and $[Re^I(PPh_3)(PF_3)(dien)]^+$, were synthesized as their triflate salts and combined with electrophiles (HOTf, $CH_2(OMe)_2$) to form $\eta^3$-allyl complexes. Treatment of these $\pi$-allyl complexes with the mild carbon nucleophile 1-methoxy-2-methyl-1-(trimethylsiloxy)propene (MMTP) followed by decomplexation affords substituted $\eta^2$-cyclopentene derivatives with excellent regio- and stereocontrol. Deuteration and NOE studies for the $\pi$-allyl complexes along with stereochemical analysis of the organic products confirm that both electrophilic and nucleophilic addition occurs exclusively from the exo face of the ring (opposite to metal coordination) for all three systems.*

Although $\eta^4$-coordinate triene complexes have been observed to react with electrophiles at an uncoordinated olefinic carbon,[1] the analogous reaction for a simple $\eta^2$-diene is far less common.[2] Electrophilic additions to $\eta^4$-dienes have been reported, but the commonly invoked reaction mechanism for this process involves electrophilic addition (typically a proton) to the metal followed by transfer to the *endo* face of the diene.[3] As a $\pi$-base, pentaammineosmium(II) has demonstrated an ability to activate $\eta^2$-coordinated aromatic $\pi$ systems toward electrophilic addition,[4] and we questioned whether this or other electron-rich 16e$^-$ systems might promote the reaction of unactivated dienes toward the direct addition of an electrophile.[5] Herein we describe the reactions of an $\eta^2$-cyclopentadiene ligand with a Brønsted acid and a carbon electrophile (an acetal) for three $d^6$-transition-metal systems: $\{Os(NH_3)_5\}^{2+}$, $\{Ru(NH_3)_5\}^{2+}$, and $\{Re(dien)(PPh_3)(PF_3)\}^+$ (Figure 1; all complexes are isolated as their triflate salts).[6]

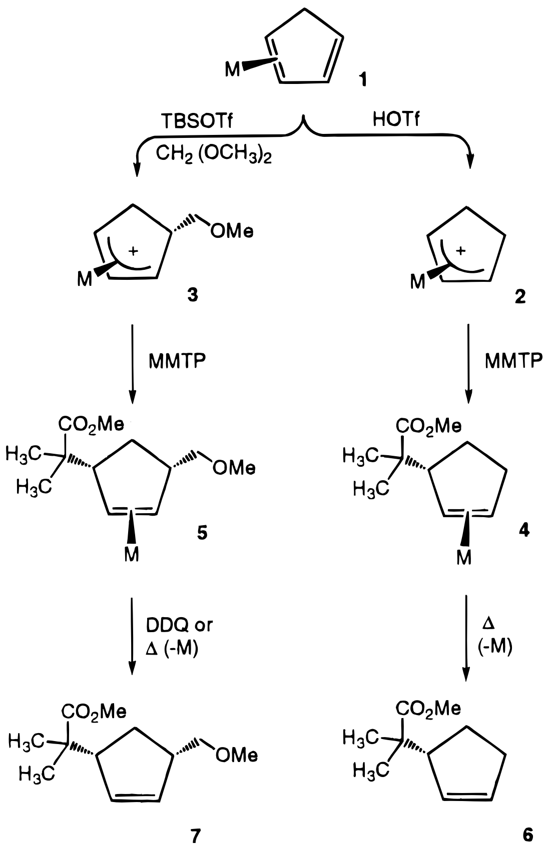

**Figure 1.** Reaction scheme for $\eta^2$-diene complexes where (a) M = $\{Os(NH_3)_5\}^{2+}$, (b) M = $\{Ru(NH_3)_5\}^{2+}$, and (c) M = $\{fac\text{-}Re(dien)(PPh_3)(PF_3)\}^+$ (all complexes isolated as triflate salts).

Desiring the simplest cyclic diene possible, we chose cyclopentadiene for our initial study. The corresponding pentaammineosmium(II) complex **1a** is readily prepared (95%) using established methods.[7] Treatment of a methanol or an acetonitrile solution of **1a** with 1.2 equiv of HOTf generates the $\pi$-allyl species **2a** in 72% isolated yield. $^1$H and $^{13}$C spectral features are typical for a symmetrical $\pi$-allylic species[8] and are in good agreement

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[1] Brookhart, M.; Volpe, A. F., Jr.; Yoon, J. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: Oxford, U.K., 1991; Vol. 4, Chapter 3.5.

[2] (a) Pearson, A. J.; Srinivasan, K. *J. Org. Chem.* **1992**, *57*, 3965. (b) Brookhart, M.; Noh, S. K.; Timmers, F. J.; Hong, Y. H. *Organometallics* **1988**, *7*, 2458. (c) Johnson, B. F. G.; Lewis, J.; Randall, G. L. P. *Chem. Commun.* **1969**, 1273.

[3] (a) Johnson, B. F. G.; Lewis, J.; Yarrow, D. J. *J. Chem. Soc., Dalton Trans.* **1972**, 2084. (b) Pearson, A. J. *Metallo-organic Chemistry*; Wiley: New York, 1985; p 267.

[4] (a) Kopach, M. E.; Gonzalez, J.; Harman, W. D. *J. Am. Chem. Soc.* **1991**, *56*, 4321. (b) Hodges, L. M.; Gonzalez, J.; Myers, W. H.; Koontz, J. I.; Harman, W. D. *J. Org. Chem* **1995**, *60*, 2125. (c) Kolis, S. P.; Gonzales, J.; Bright, L. M.; Harman, W. D. *Organometallics* **1996**, *15*, 245.

[5] Shepherd has demonstrated that addition of $Br_2$ occurs on the uncoordinated portion of butadiene, but this reaction readily occurs for organic olefins. See: Elliot, M. G.; Shepherd, R. E. *Inorg. Chem.* **1988**, *27*, 3332.

[6] The complex $[Os(NH_3)_5(\eta^2\text{-1,3-cyclohexadiene})]^{2+}$ was previously reported to undergo protonation to form an allyl species; however, nothing was reported about the mechanism. See: Harman, W. D.; Hasegawa, T.; Taube, H. *Inorg. Chem.* **1991**, *30*, 453.

[7] Synthesis and characterization of **1a**: $Os(NH_3)_5(OTf)_3$ (3.02 g, 4.18 mmol) was reduced ($Mg^0$, 3.02 g) in a solution of cyclopentadiene (3.15 g, 49.2 mmol) and DMAc (2.95 g). Yield upon precipitation in $CH_2Cl_2$: 2.54 g (95%). $^1$H NMR ($CD_3CN$): $\delta$ 6.32 (dd, $J$ = 6.8 Hz, 1.9 Hz, 1H), 5.97 (dd, $J$ = 6.8 Hz, 2.1 Hz, 1H), 4.65 (d, $J$ = 5.9 Hz, 1H), 4.13 (d, $J$ = 5.9 Hz, 1H), 4.10 (br s, 3H), 2.89 (br s, 12H), 2.45 (m, 1H), 2.38 (m, 1H). Anal. Calcd for $C_7H_{27}N_5O_6F_6S_2Os$: C, 13.15; H, 3.31; N, 10.95. Found: C, 12.96; H, 3.60; N, 10.78.

[8] Charaterization data for **2a**: $^1$H NMR ($CD_3CN$) $\delta$ 5.72 (d, $J$ = 2.9 Hz, 1H), 4.99 (t, $J$ = 2.9 Hz, 1H), 4.88 (br s, 3H), 3.71 (br s, 12H), 2.94 (d, $J$ = 16.2 Hz, 1H), 1.63 (d, $J$ = 16.2 Hz, 1H); $^{13}$C NMR ($CD_3CN$) $\delta$ 94.41 (CH), 83.63 (CH), 31.86 ($CH_2$). Anal. Calcd for $C_8H_{22}N_5O_9S_3F_9Os$: C, 12.17; H, 2.81; N, 8.87. Found: C, 11.95; H, 2.47; N, 9.14.

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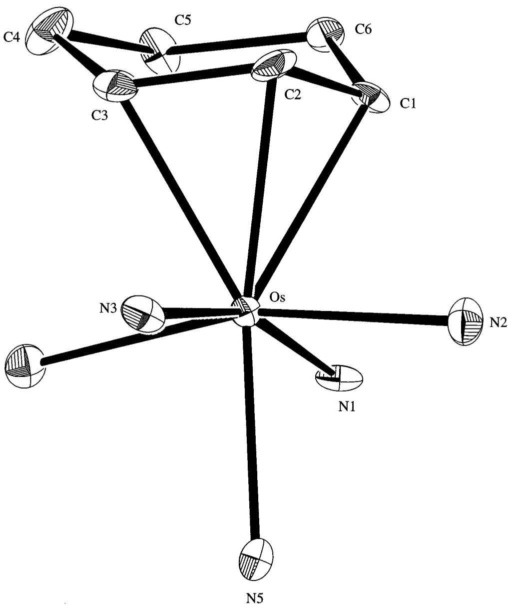
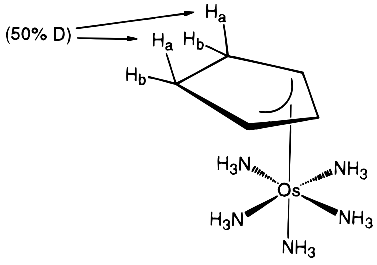


**Figure 2.** ORTEP drawing for the $\pi$-allyl complex $[Os(NH_3)_5(\eta^3\text{-}C_6H_9)]^{3+}$ **(8)**. Selected bond lengths (Å): Os−C(1), 2.25 (1); Os−C(2), 2.19(1); Os−C(3), 2.26(1); C(1)−C(2), 1.40(2); C(2)−C(3), 1.42(2). Selected bond angles (deg): C(1)−C(2)−C(3), 111(1).

with what has been reported for the cyclohexadiene analog, **8** (Figure 2).[6] Although efforts to grow a crystal of **2a** suitable for structural analysis were unsuccessful, well-formed crystals of **8** were eventually obtained from acetonitrile solution and an X-ray structure determination was carried out.[9] Carbon−metal bond lengths are virtually identical (2.25, 2.26 Å) for the two terminal carbons (Figure 2), while the central carbon is drawn in considerably closer to the osmium (2.19 Å).

To establish the facial selectivity of diene protonation, a sample of **1a** was treated with DOTf in $CD_3OD$ to generate **2a**-$d_1$. A $^1H$ NMR spectrum ($CD_3CN$) establishes that only one of the four diastereotopic methylene positions incorporates a significant amount of deuterium. For **2a**-$d_1$, the overall intensity of the resonance $H_a$ is lowered by half, while the signal for $H_b$ becomes a superposition of the original doublet (1.67 ppm; 3.7 Hz) and a new a singlet (1.62 ppm). When the *cis*-ammine signal is irradiated, an 11% NOE is measured for $H_b$. Taken together, these observations confirm that protonation occurs from the *exo* face of the diene.[10]



**2a**

In a similar manner, a $\pi$-allyl species was prepared from the cyclopentadiene complex **1a** with a carbon electrophile.[11] Treatment of an acetonitrile solution of **1a** with the acetal dimethoxymethane (1.2 equiv) and Lewis acid (TBSOTf, 1.1 equiv) results in the formation of $\pi$-allyl **3a**. A full spectroscopic analysis[12] of **3a** reveals the methoxymethylcyclopentadienium species shown in Figure 1, where electrophilic addition again occurs to the *exo* face of the diene. Subsequent treatment of either allyl species **2a** or **3a** with a mild carbon nucleophile[13] generates a substituted cyclopentene complex. For example, when a solution of **2a** or **3a** is combined with 1-methoxy-2-methyl-1-(trimethylsiloxy)-propene (MMTP), alkene complexes are formed (**4a** (79%) and **5a** (81%), respectively) that upon oxidation with DDQ (0.6 equiv) release the alkylated cyclopentenes **6** (70%) and **7** (75%), respectively. In the latter case, nucleophilic addition occurs to the allyl species to form a single regio- and diastereomer (>10:1) that $^{13}C$ and $^1H$ NMR, COSY, and NOE data indicate is the *cis*-3,5-disubstituted cyclopentene product.

The weaker $\pi$-donor properties of ruthenium make protonation of the diene complex **1b** considerably more difficult than its heavy-metal congener.[14] Whereas **1a** can be protonated in methanol, the formation of the $\pi$-allyl species **2b** requires protonation of the diene complex **1b** in acetonitrile at −40 °C. Spectral features for **2b** (−40 °C, $CD_3CN$) correlate well with those of **2a**.[15] Although attempts to isolate **2b** failed due to its thermal instability, it can be trapped by a suitable nucleophile to generate substituted cyclopentenes. For example, when a solution of **1b** (−50 °C) is treated with triflic acid followed by MMTP, the cyclopentene complex **4b** is recovered in good yield (83%). Heating **4b** (30 min, 60 °C) delivers the organic cyclopentene **6** in 63% yield. Repeating this sequence for **1b** with dimethoxymethane (TBSOTf; −45 °C) delivers the disubstituted cyclopentene complex (**5b**) that when heated yields the *cis*-3,5-disubstituted cyclopentene **7** as a single regioisomer with good stereoselectively (>10:1) in overall 83% yield from **1b**.

Hoping to show this novel diene reactivity for a metal outside of group VIII, our focus shifted to rhenium, where our intention was to examine a system with similar electronic structure to the pentaammineosmium(II) moiety. The system $\{fac\text{-}Re(dien)(PPh_3)(PF_3)\}^+$ is isoelectronic with the osmium system, shows a similar electrochemical profile,[16] and does not have chemically accessible electrons on its ancillary ligands that might be a target for an electrophile. When a sample of $[fac\text{-}Re(dien)(PPh_3)(PF_3)(OTf)](OTf)$[17] is reduced with $Mg^0$ in the presence of cyclopentadiene, the compound [*fac*-

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(9) Crystal data for **8**, $[Os(NH_3)_5(C_6H_9)](OTf)_3\cdot 2CH_3CN$: $C_{11}H_{24}F_9N_6O_9S_3Os$; $M = 841.7$; triclinic, $P\bar{1}$ (No. 2); $a = 12.105(4)$, $b = 15.648(6)$, $c = 8.457(3)$ Å; $\alpha = 105.46(2)°$, $\beta = 102.71°$, $\gamma = 103.97°$; $V = 1427$ Å$^3$; $Z = 2$; $D_{calc} = 1.96$ g cm$^{-3}$. Unique reflections: 5015. $R = 0.064$, $R_w = 0.090$, and GOF = 2.46.

(10) *Exo* addition of electrophiles is also observed with aromatic systems bound to pentaammineosmium(II). See ref 4.

(11) Preliminary evidence suggests that Michael acceptors, acetals, and alkyl triflates, all react with $\eta^2$-diene complexes of osmium(II).

(12) These experiments include $^1H$, $^{13}C$, DEPT, and NOE.

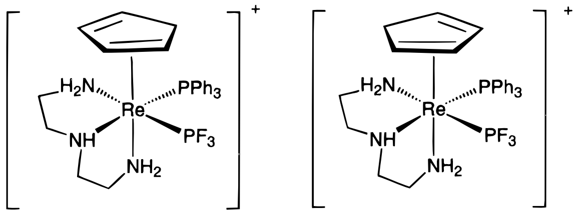
(13) Nucleophiles that react with **2**, **3**, or **8** include silated enols, hydride, and cyanide reagents. Spera, M. L.; Lopez, K. W.; Harman, W. D. Preliminary results.

(14) Synthesis of **1b** is accomplished by reducing $Ru(NH_3)_5(OTf)_3$ in acetone and CpH with Zn/Hg amalgam. Yield = 79%. See Supporting Information.

(15) Characterization of **2b**: Partial $^1H$ NMR ($CD_3CN$, −40 °C) $\delta$ 5.18 (m, 1H), 5.02 (m, 1H), 4.75 (br s, 3H), 3.38 (dd, $J = 20.2$ Hz, 4.9 Hz, 1H), 2.92 (br s, 12H). One proton resonance was not assigned.

(16) For a number of examples, the reduction potentials of $[Os(NH_3)_5L]^{2+}$ and $[Re(dien)(PPh_3)(PF_3)(L)]^+$ are within 200 mV of each other. See ref 17.

(17) Chin, R. M.; Dubois, R. H.; Helberg, L. E.; Sabat, M.; Bartucz, T. Y.; Lough, A. J.; Morris, R. H.; Harman, W. D. Manuscript submitted for publication.



**1c**

**Figure 3.** Diastereomers for the diene complex **1c**.

Re(dien)(PPh$_3$)(PF$_3$)($\eta^2$-CpH)](OTf) (**1c**) is isolated (59%) as a 5:2 equilibrium mixture of diastereomers (Figure 3).[18] Treatment of this mixture with triflic acid in methanol or acetonitrile generates the $\pi$-allyl complex **2c** (84%).[19] In a similar manner, when diene complex **1c** is combined with dimethoxymethane (22 °C) and TBSOTf with 2,6-di-*tert*-butylpyridine, a 5:2 diastereomeric mixture of allyl species **3c** (86%) is formed, consistent with the original ratio of diene diastereomers.[20] Treatment of the allyl species **2c** and **3c** with MMTP (CH$_3$CN) generates the cyclopentene complexes **4c** (62%) and **5c** (59%), respectively. In the latter case, the cyclopentene complex is isolated as a 5.5:1 mixture of isomers.[21] When **5c** is heated in an acetonitrile solution, compound **7** is recovered as the same stereoisomer (de >90%) recovered from ruthenium or osmium.[22] That **7** is recovered exclusively as the *cis* isomer confirms that electrophilic addition occurs from the *exo* face in the rhenium system as is observed for the group VIII metals.

For three complimentary d$^6$ octahedral transition-metal systems we have shown that $\eta^2$-dienes undergo direct electrophilic addition of both a proton and carbon electrophiles to form cationic $\pi$-allyl complexes. Given the general reactivity of allyl cations with mild nucleophiles, this sequential stereocontrolled addition of electrophile and nucleophile to an $\eta^2$-diene complex is potentially a useful new synthetic tool for the stereoselective preparation of substituted cycloalkenes. Work in our laboratories is currently focusing on the scope of this reaction sequence and the possibility of enantioselective transformations with the described rhenium system.

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**Supporting Information Available:** Text giving full experimental procedures and characterizations for all compounds described in this account and complete tables of crystallographic data and an ORTEP diagram for **8** (13 pages). Ordering information is given on any current masthead page.

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(18) Synthesis and characterization of **1c:** *fac*-[Re(OTf)(PPh$_3$)(PF$_3$)(dien)](OTf) (4.56 g, 4.86 mmol), cyclopentadiene (5.2 g, 78.8 mmol), and Mg$^0$ were stirred in DME (35 mL; 2 h) and then filtered. The filtrate was added to Et$_2$O to precipitate the product as a white solid. Yield: 2.46 g (59%, 5:2 mixture of two isomers). $^1$H NMR (CD$_3$CN, both isomers): $\delta$ 7.64−7.31 (m, 30H), 6.23 (br s, 1H), 6.13 (br s, 1H), 5.93 (m, 1H), 5.27 (m, 1H), 5.09 (m, 1H), 4.00 (m, 1H), 3.84 (m, 1H), 3.69−2.29 (m, 12H), 2.18 (m, 1H), 2.02−1.64 (m, 3H). Anal. Calcd for $C_{28}H_{34}F_6O_3N_3P_2ReS$: C, 39.34; H, 4.01; N, 4.92. Found: C, 39.82; H, 4.28; N, 4.90.

(19) Characterization of **2c**: 84% yield from the protonation (HOTf) of **1c** in acetonitrile. $^1$H NMR (CD$_3$CN): $\delta$ 7.66−7.49 (m, 15 H), 5.78 (br s, 1 H), 4.60 (br s, 1 H), 4.49 (br s, 1 H), 4.43 (br s, 1 H), 4.25 (br s, 1 H), 4.02 (br s, 1 H), 3.96−3.79 (m, 2H), 3.26−3.04 (m, 5H), 3.03−2.75 (m, 2H), 2.57 (m, 1H), 2.41 (m, 1H), 0.93 (dd, $J$ = 6.1 Hz, 15.9 Hz, 1H). Anal. Calcd for $C_{29}H_{35}F_9O_6N_3P_2ReS_2$: C, 34.66; H, 3.51; N, 4.18. Found: C, 34.63; H, 3.15; N, 4.10.

(20) Characterization of **3c** (both isomers): 86% yield from **1c**. $^1$H NMR (CD$_3$CN): $\delta$ 7.64−7.39 (m, 15H), 6.04 (br s, 1H), 5.92 (br s, 1H), 4.74 (br s, 1H), 4.68 (br s, 1H), 4.42 (br s, 1H), 4.35 (br s, 1H), 4.16 (br s, 1H), 3.98 (br s, 1H), 3.79 (br s, 1H), 3.66 (m, 1H), 3.24 (s, 3H), 3.02 (s, 3H), 3.31−2.71 (m, 20H), 2.40−2.03 (m, 9H), 1.25 (m, 3H). Anal. Calcd for $C_{29}H_{39}N_3F_9O_7P_2S_2Re$: C, 33.99; H, 3.84; N, 4.10. Found: C, 33.71; H, 3.96; N, 4.11.

(21) The ratio of isomers in isolated **5b** is significantly different than the 5:2 ratio of its precursor. However, only 59% of the product is isolated from solution, and it is likely that one diasteromer is less soluble than the other.

(22) Characterization of **7** (75% from 5a): $^1$H NMR (CDCl$_3$) $\delta$ 5.69 (m, 1H), 5.65 (m, 1H), 3.66 (s, 3H), 3.35 (s, 3H), 3.29 (m, 2H), 3.06 (m, 1H), 2.94 (m, 1H), 2.08 (m, 1H), 1.2 (m,1H), 1.16 (s, 3H), 1.10 (s, 3H); $^{13}$C NMR (CDCl3) $\delta$ 177.95 (CO), 133.02 (CH), 132.37 (CH), 77.19 (CH$_2$), 72.42 (CH), 58.92 (CH), 53.79 (CH$_3$), 51.66 (CH$_3$), 44.43 (C), 29.12 (CH$_2$), 22.79 (CH$_3$), 22.21 (CH$_3$). Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.62; H, 9.88. The regio- and stereochemistry was confirmed by 1D-NOE, COSY, and $^1$H−$^1$H decoupling data.