

Registry No. 3, 139071-24-2; *c*-C₃H₅CHO, 1489-69-6; W₂(ONP)₆(py)₂, 88608-50-8; W₂(ONP)₆(μ-CH(C₃H₅))(O)(py), 139071-23-1; 2-cyclohexenone, 930-68-7.

Supplementary Material Available: NMR and crystallographic data comprised of a summary of data collection and refinement, VERSORT and stereodrawings, tables of atomic coordinates, and complete listings of bond distances and angles (32 pages); listings of observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

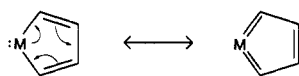
Osmacyclopentatriene Complexes: Structural Characterization of [Os(C₄Me₄)(en)₂](CF₃SO₃)₂

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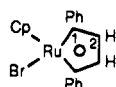
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Metallacyclopentadiene complexes have attracted considerable interest, because they are considered important intermediates in alkyne cyclization.² However, very few metallacyclopentatriene complexes which, as shown, are resonance forms of metallacyclopentadienes have been prepared and characterized.^{3,4}



- (1) (a) Stanford University. (b) University of California at Davis.
(2) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987; Chapters 9 and 18. (b) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539. (c) Maitlis, P. M. *Pure Appl. Chem.* **1972**, *30*, 427. (d) For a theoretical study of metallacyclopentadienes, see: Thorn, D. L.; Hoffmann, R. *Nouv. J. Chim.* **1979**, *3*, 39.
(3) (a) One planar metallacycle of the formula (η⁵-C₅H₅)Ru(C₄Ph₂H₂)Br has been isolated: Albers, M. O.; deWaal, P. J. A.; Liles, D. C.; Robinson, D. J.; Singleton, E.; Wiege, M. B. *J. Chem. Soc., Chem. Commun.* **1986**, 1680. The authors named this compound as metallacyclopentatriene. However, the



structural evidence suggests that it may be better described as a five-membered aromatic metallacycle, a resonance structure between metallacyclopentadiene and metallacyclopentatriene for the following reasons: (i) The bond distances of C(1)-C(2) [1.403 (8) Å] and C(2)-C'(2) [1.377 (12) Å] are almost identical. In other metallacyclopentadiene compounds, the difference between the carbon-carbon single bond and double bond is ca. 0.10-0.15 Å: Mague, J. T. *Inorg. Chem.* **1970**, *9*, 1610. Gastinger, R. G.; Rausch, M. D.; Sullivan, D. A.; Palenik, G. J. *J. Am. Chem. Soc.* **1976**, *98*, 719. Gastinger, R. G.; Rausch, M. D.; Sullivan, D. A.; Palenik, G. J. *J. Organomet. Chem.* **1976**, *117*, 355. Suzuki, H.; Itoh, K.; Ishii, Y.; Simon, K.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 8494. Atwood, J. L.; Hunter, W. E.; Alt, H.; Rausch, M. D. *J. Am. Chem. Soc.* **1976**, *98*, 2454. O'Connor, J. M.; Pu, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 6232. (ii) The 1.942 (6) Å Ru-C(1) bond distance is in the range of the longest bond lengths of the previously reported Ru-C double bond length, 1.83-1.91 Å: Clark, G. R. *J. Organomet. Chem.* **1977**, *134*, 51. Hitchcock, P. B.; Lappert, M. F.; Pye, P. L.; Thomas, S. J. *Chem. Soc., Dalton Trans.* **1979**, 1929. Selegue, J. P. *Organometallics* **1982**, *1*, 217. Bruce, M. I.; Wong, F. S.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1982**, 2203. Selegue, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 5921. Crocker, M.; Green, M.; Orpen, A. G.; Neumann, H.-P.; Schaverien, C. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1351. (iii) The chemical shift of the two hydrogens on the metallacycle at δ 7.82 is significantly downfield of the vinyl proton signal at δ 6.8 in 1,1,4,4-tetraphenyl-1,3-butadiene: Weast, R. C.; Grasselli, J. G. *Handbook of Data on Organic Compounds*, 2nd ed.; CRC Press: Boca Raton, FL, 1989; Vol. 1, p 464. (b) For examples of delocalization in the metallacyclopentadiene structure, see: Mague, J. T. *Inorg. Chem.* **1970**, *9*, 1610. Pierpont, C. G.; Downs, H. H.; Itoh, K.; Nishiyama, H.; Ishii, Y. *J. Organomet. Chem.* **1976**, *124*, 93.

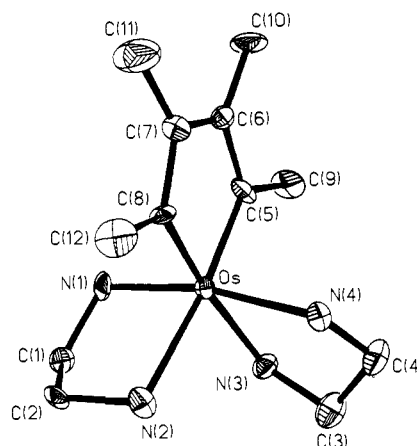


Figure 1. Molecular structure and labeling scheme for **1**: Os-N(1) 2.101 (7), Os-N(2) 2.239 (7), Os-N(3) 2.274 (8), Os-N(4) 2.120 (7), Os-C(5) 1.940 (8), Os-C(8) 1.931 (8), C(5)-C(6) 1.461 (13), C(6)-C(7) 1.357 (12), C(7)-C(8) 1.448 (12) Å; N(1)-Os-N(2) 78.3 (3), N(1)-Os-N(3) 92.8 (3), N(2)-Os-N(3) 84.2 (3), N(1)-Os-N(4) 168.0 (3), N(1)-Os-C(5) 94.9 (3), N(2)-Os-C(5) 172.9 (3), N(3)-Os-C(5) 98.5 (3), N(4)-Os-C(5) 95.4 (3), N(1)-Os-C(8) 94.9 (3), N(2)-Os-C(8) 96.9 (3), N(3)-Os-C(8) 172.2 (3), N(4)-Os-C(8) 92.6 (3), C(5)-Os-C(8) 81.3 (4), Os-C(5)-C(6) 116.1 (6), C(5)-C(6)-C(7) 111.9 (7), C(6)-C(7)-C(8) 115.3 (8), Os-C(8)-C(7) 115.1 (6)°.

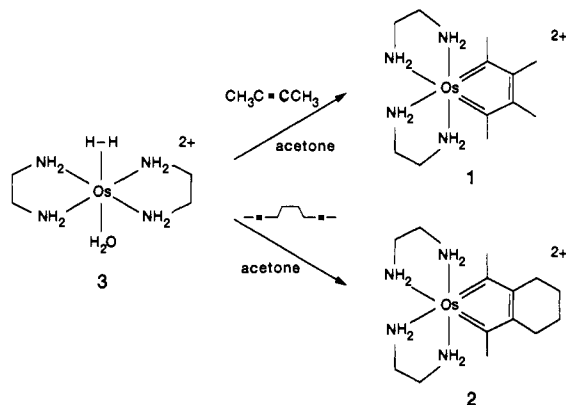
In this communication, we wish to report the synthesis and characterization of two novel metallacyclopentatrienes, *cis*-[Os(C₄Me₄)(en)₂]²⁺ (**1**) and *cis*-[Os(C₁₀H₁₄)(en)₂]²⁺ (**2**), prepared as the bis(trifluoromethanesulfonate) salts (en = ethylenediamine). The method of preparation which depends on the reaction of alkynes with an η²-dihydrogen complex of bis(ethylenediamine)osmium(II) merits special mention. In earlier work in this laboratory,^{5a} it was shown that a compound prepared over two decades ago,^{5b} and then described as dihydridobis(ethylenediamine)osmium(IV), has a *trans* arrangement of the en ligands and that the purported two hydrides actually constitute an η²-H₂ unit occupying one face of the plane. The opposite face is occupied by a ligand which, in the absence of a more nucleophilic candidate, is a molecule of the solvent. It was also shown that the dihydrogen is readily replaced by strong π acid ligands.

When an acetone solution of *trans*-[Os(en)₂(η²-H₂)(H₂O)]-(CF₃SO₃)₂ (**3**) (0.53 mmol, 0.13 M) and 2-butyne (7.2 mmol) is heated at 59 °C for 21 h, the yellow green solution turns dark green. A new compound, [Os(C₄Me₄)(en)₂](CF₃SO₃)₂ (**1**), is isolated in 95% yield by precipitation with ether. The ¹H NMR spectrum of **1** in acetone-*d*₆ shows four broad peaks for amine protons at δ 7.74, 6.55, 6.27, 6.11 and four multiplets for the methylene protons at δ 3.12, 3.96, 2.75, 2.57, which indicates that the original planar symmetry has been reduced to C₂, the two *trans*-ethylenediamine ligands of **3** having rearranged to the *cis* position. Two singlets at δ 2.22 and 0.60, each corresponding to six protons, are observed for the methyl groups; that is, 2 equiv of the alkyne molecules have coupled on the metal center to form a metallacycle. The strong π back-bonding tendency of osmium(II) amine moieties^{5c} suggests that the conventional metallacyclopentadiene structure, which has two M-C single bonds, would be disfavored in comparison to the metallacyclopentatriene structure with two Os-C double bonds. The ¹³C{¹H} NMR spectrum of **1** does show a singlet at δ 266.6, which is consistent with the existence of carbene carbons in the proposed osmacyclopentatriene structure. An intramolecular alkyne cyclization also occurs to generate complex **2**, *cis*-[Os(C₁₀H₁₄)(en)₂](CF₃SO₃)₂, when **3** (0.206 mmol, 51.5 mM) is treated with 2,8-

- (4) Two nonplanar metallacyclopentatriene complexes of early transition elements were reported: Hirpo, W.; Curtis, M. D. *J. Am. Chem. Soc.* **1988**, *110*, 5218. Kerschner, J. L.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1988**, *110*, 8235.

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decadiyne (45 μ L) in acetone at 59 °C for 2 days. The product is isolated with a crude yield of \sim 90% by the addition of ether. It contains about 10% of other products, which presumably result from intermolecular cyclization. A singlet at δ 0.52 (6 H) in the ^1H NMR spectrum of **2** can only be assigned to the α -methyl groups. Therefore, the upfield singlet at δ 0.60 (6 H) observed in the ^1H NMR spectrum of **1** can be also attributed to the resonance of the α -methyl groups, and the singlet at δ 2.22 (6 H) then must be the resonance of the β -methyl groups. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (acetone- d_6) of **2**, the bis-carbene carbon signals are found at δ 265.2.



For further structural characterization, a single-crystal X-ray diffraction study was performed on **1** (Figure 1).⁶ The Os_4 unit is shown to be planar. The $\text{Os}-\text{C}(5)$ and $\text{Os}-\text{C}(8)$ bond distances of 1.940 (8) and 1.931 (8) Å are very close to the 1.90 Å $\text{Os}-\text{C}$ bond distance observed in an osmium vinylidene complex.⁷ The $\text{C}(6)-\text{C}(7)$ bond distance of 1.357 (12) Å is a typical carbon-carbon double bond, and the $\text{C}(5)-\text{C}(6)$ and $\text{C}(7)-\text{C}(8)$ bond distances of 1.461 (13) and 1.448 (12) Å are typical carbon-carbon single bonds as observed in a butadiene structure (1.34 and 1.48 Å, respectively).⁸ We conclude that the osmium metallacycle is a localized planar metallacyclopentatriene complex.⁹

A three-stage hydrogen-deuterium exchange is observed when complex **1** is dissolved into D_2O . A D_2O solution of **1** (7.3×10^{-3} mmol, 10.4 mM) kept under N_2 is followed by ^1H NMR spectroscopy.¹⁰ In less than 2 min, the ^1H NMR spectrum shows that the two most downfield proton signals observed in acetone- d_6 , corresponding to four amine protons, are now absent. After \sim 24 h, the peaks at δ 5.89 and 5.67 of the other four amine protons disappeared. Then, while the intensity of the singlet at δ 0.267, the α -methyl resonance, is decreasing, a broad triplet at δ 0.178 ($J_{\text{HD}} = 1.9$ Hz) is slowly growing. In 7 days, \sim 20% of the α -methyl is monodeuterated.¹¹ Here, we notice an unusually large

upfield isotope shift ($\Delta\delta = 0.089$ ppm) from the singlet to the triplet.¹² The β -methyl resonance at δ 2.09 does not change during this period. The presence of acidic protons in the α -methyl groups demonstrated by the hydrogen-deuterium exchange experiment is an indication of the carbene character of the α -metallacycle carbons.¹³

A metallacyclopentatriene is composed of two cis carbene carbons in an unsaturated metallacycle. The study of this class of compounds can provide new insights on both carbene and metallacycle reactivity. An investigation of the chemistry is currently underway, the results of which will be reported later.

Acknowledgment. Financial support from the National Institutes of Health (GM-13638-25) and from Shin-Etsu Chemical Co. for partial support of Dr. Tai Hasegawa is gratefully acknowledged. We also thank Prof. H. Hope at the University of California—Davis for providing the X-ray facility.

Registry No. **1**, 139198-96-2; **2**, 139198-98-4; **3**, 139242-58-3; $\text{CH}_3\text{C}=\text{CCH}_3$, 503-17-3; $\text{CH}_3\text{C}=\text{C}(\text{CH}_2)_4\text{C}=\text{CCH}_3$, 4116-93-2.

Supplementary Material Available: Listings of analytical and spectroscopic data for compounds **1** and **2** and tables of atomic coordinates and equivalent isotropic displacement coefficients, bond lengths, bond angles, anisotropic displacement coefficients, hydrogen atom coordinates, and isotropic displacement coefficients (6 pages); table of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

(11) In the presence of base (e.g., propylamine), the α -methyl group is completely deuterated in minutes under similar conditions.

(12) (a) Substitution of a proton with a deuterium atom in a methyl group usually gives an upfield isotope shift of 0.01–0.02 ppm in the ^1H NMR spectrum: Batiz-Hernandez, H.; Bernheim, R. A. *Prog. Nucl. Magn. Reson. Spectrosc.* **1967**, *3*, 63. (b) An isotope shift as large as 0.05 ppm is observed in a bimetallic malonyl system: O'Connor, J. M.; Uhrhammer, R. *J. Am. Chem. Soc.* **1988**, *110*, 4448.

(13) Protons on the α -carbon of a Fischer carbene complex are acidic: ref 2a, p 128.

Modeling Fragments for the ab Initio Determination of Electron Density in Polypeptides. An Experimental and Theoretical Approach to the Electron Distribution in Leu-enkephalin Trihydrate

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The electron density of relatively large biomolecules is now accessible to X-ray diffraction techniques. The experience gathered in the last 20 years on smaller systems has shown that ab initio SCF calculations carried out with large, polarized basis sets could provide a near quantitative agreement with properly refined experimental maps.¹ Unfortunately, the dependence of

(6) Crystal data for **1** (120 K): $\text{C}_{14}\text{H}_{16}\text{N}_4\text{OsF}_6\text{O}_6\text{S}_2$, orthorhombic, P_{21} ; $a = 14.208$ (4) Å, $b = 26.409$ (7) Å, $c = 12.723$ (3) Å, $V = 4774$ (2) Å³, $Z = 8$, $D_{\text{calc}} = 1.961$ g cm⁻³, $\mu = 5.597$ mm⁻¹. A dark green hexagonal prism specimen (0.40 \times 0.30 \times 0.30 mm) was used for data collection (Siemens P3RA, $0.0^\circ < 2\theta < 55.0^\circ$, Mo $K\alpha$). Of 6126 reflections collected, 5524 were independent, and 3869 with $F_o > 4.0\sigma(F)$ were considered observed and were empirically corrected for absorption by using the XABS program (this program generates an absorption correction tensor based on F_o and F_c differences. Hope, H.; Moezzi, B. Chemistry Department, University of California at Davis). The atoms were located by Patterson methods and refined by full-matrix least-squares. Hydrogen atoms were calculated and refined by riding model with fixed isotropic U : $R = 4.43\%$, $R_w = 5.20\%$ ($R = \sum |F_o| - |F_c| / \sum |F_o|$; $R_w = \sum |F_o| - |F_c| / \sum |F_o| w^{1/2}$), all data $R = 7.06\%$, GOF = 0.72. All computer programs and sources of scattering factors are contained in SHELXL PLUS (G. M. Sheldrick, a program for crystal-structure determination, version 4.0, 1989, Siemens Analytical X-ray Instruments, Madison, WI).

(7) Roper, W. R.; Waters, J. M.; Wright, L. J.; vanMeurs, F. *J. Organomet. Chem.* **1980**, *201*, C27.

(8) Stoeckel, B. P. *Advances in Spectroscopy*; Thompson, H. W., Ed.; Interscience Publishers: New York, 1959; Vol. 1, p 148.

(9) To compare the structure of **1** with its isoelectronic Ir(III) metallacyclopentadiene complexes, see: O'Connor, J. M.; Pu, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 6232.

(10) The ^1H NMR resonances of **1** in D_2O are shifted upfield by ca. 0.1–0.4 ppm from that in acetone- d_6 .

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[‡] Laboratoire de Chimie Quantique.

(1) (a) Stevens, E. D.; Rys, J.; Coppens, P. *J. Am. Chem. Soc.* **1978**, *100*, 2324–2328. (b) Stevens, E. D.; Rys, J.; Coppens, P. *J. Am. Chem. Soc.* **1977**, *99*, 265–267. (c) Breitenstein, M.; Dannöhl, H.; Meyer, H.; Schweig, A.; Seeger, R.; Seeger, U.; Zittlau, W. *Int. Rev. Phys. Chem.* **1983**, *3*, 335–391. (d) Souhassou, M.; Lecomte, C.; Ghermani, N.-E.; Rohmer, M.-M.; Wiest, R.; Bénard, M.; Blessing, R. H. *J. Am. Chem. Soc.*, in press.