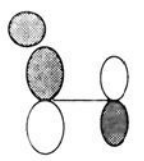
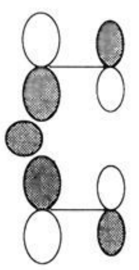
has a π orbital and a π^* orbital. As shown in **6**, the interaction of a hydride HOMO with the LUMO of one electrophilic C=X species occurs with an obtuse angle of attack, to maximize the overlap of these orbitals and to minimize interaction of the hydride HOMO with the C=X HOMO.[15] The corresponding orbital interaction in the transition structure for hydride transfer is the interaction between the hydride HOMO and the bonding combination of π^* orbitals of both C=X groups, shown in **7**. This interaction is increased by the overlap between the two π^* orbitals, which occurs principally at carbon. This overlap lowers the energy of the composite LUMO, decreases the energy difference between the hydride HOMO and the composite LUMO, and increases the interaction energy. The $\pi^*-\pi^*$ overlap is best in the syn bent structure, **7**, while it is poor in the two linear structures, **8** and **9**. The variation of CHC angle in the anti structure, **9**, does not influence molecular orbital overlaps appreciably. Therefore, nonlinearity is not important in the anti structures, and additional stabilization by $\pi^*-\pi^*$ interaction does not occur.

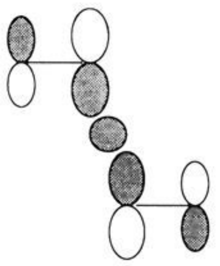


6



7

8



9

Complications may occur because the syn structure may be destabilized by charge or dipolar interactions, while the anti structure is stabilized by dipole interactions. Consequently, the general trends uncovered here for this reaction may have to be altered for other charge types.

Acknowledgment. We are grateful to the National Science Foundation for financial support of this research, to Professor Gordon Hamilton for suggesting that we look for a pericyclic component to hydride transfers, and to Professors Lee C. Allen and Richard J. Schowen for stimulating discussions of this problem.

---

(1) Wu, Y.-D.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 906.

(2) *Applications of Biochemical Systems in Organic Chemistry*; Jones, J. B., Sih, C. J., Perlman, D., Eds.; Wiley: New York, 1976.

(3) Meyers, A. I.; Openlaender, T. *J. Am. Chem. Soc.* **1986**, *108*, 1989 and references therein.

(4) Binkley, J. S.; Frisch, M.; Krishnan, R.; DeFrees, D.; Schlegel, H. B.; Whiteside, R. A.; Fluder, E.; Seeger, R.; Pople, J. A. GAUSSIAN 82, Carnegie-Mellon University, Pittsburgh, PA.

(5) Huttley, B. G.; Mountain, A. E.; Williams, I. H.; Maggiora, G. M.; Schowen, R. J. *J. Chem. Soc., Chem. Commun.* **1986**, 267. Professor Schowen has informed us that the C_{2h} structure does indeed have a second imaginary frequency of 25 cm^{-1} and that the 3-21G surface is very flat in the region of this stationary point.

(6) The reaction of dihydropyridine with formaldehyde gives no transition structure with the 3-21G basis set.

(7) Van der Kerk, S. M.; Van Gerresheim, W.; Verhoeven, J. W. *Recl. Trav. Chim. Pays-Bas* **1984**, *103*, 143.

(8) Verhoeven, J. W.; Van Gerresheim, W. O.; Martens, F. M.; van der Kerk, S. M. *Tetrahedron* **1986**, *42*, 975.

(9) Powell, M. F.; Bruice, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 1041.

(10) Ohno, A.; Ikegushi, M.; Kimura, T.; Oka, S. *J. am. Chem. Soc.* **1979**, *101*, 7036.

(11) Sheldon, J. S.; Bowie, J.; Hayes, M. S. *Nouv. J. Chim.* **1984**, *8*, 79.

(12) de Kok, P. M. T.; Donkersloot, M. C. A.; van Lieu, P. M.; Meulendijks, G. H. W. M.; Bastiaansen, L. A. M.; Van Hooff, H. J. G.; Kanters, J. A.; Buck, H. M. *Tetrahedron* **1986**, *42*, 941.

(13) Dihydropyridine is planar: Raber, D. J.; Rodriguez, W. *J. Am. Chem. Soc.* **1985**, *107*, 4146.

(14) Benner, S. A.; Nambiar, K. P.; Chambers, G. K. *J. K. J. Am. Chem. Soc.* **1985**, *107*, 5513. Nambiar, K.; Stauffer, D. M.; Kolodziej, P. A.; Benner, S. A. *J. Am. Chem. Soc.* **1983**, *105*, 5886. Benner, S. A. *Experientia* **1982**, *38*, 633.

(15) Houk, K. N.; Paddon-Row, M. N.; Rondan, N. G.; Wu, Y.-D.; Brown, F. K.; Spellmeyer, D. C.; Metz, J. T.; Li, Y. Loncharich, R. J. *Science (Washington, D.C.)* **1986**, *231*, 1108 and references therein.

Multisubstitution of $Os(CO)_5$ by Ethylene: Isomeric $Os(CO)_2(C_2H_4)_3$ and a Derivative of $Os(CO)(C_2H_4)_4$[1]

Gong-Yu Kiel and Josef Takats*

Department of Chemistry, University of Alberta
Edmonton, Alberta, Canada T6G 2G2

Friedrich-Wilhelm Grevels

Max-Planck-Institut für Strahlenchemie
D-4330 Mülheim a.d. Ruhr, Federal Republic of Germany

Received August 18, 1986

Although the synthesis and isolation of a variety of mono-, bis-, and even tris-olefin derivatives of the iron triad carbonyls have been reported,[2] progress with the simplest olefin, ethylene, has been surprisingly slow. However, recent observations by Wrighton[3] have revealed hitherto unobserved multisubstitution of CO by ethylene with iron and ruthenium carbonyl complexes. In view of this work, we wish to communicate our preliminary results on $Os(CO)_5$–ethylene photochemistry which allowed the isolation and full characterization of most members of the series of ethylene complexes $Os(CO)_{5-x}(C_2H_4)_x$, $x = 1–4$.

Photolysis of $Os(CO)_5$ and ethylene in hydrocarbon solvent gives, in a wavelength-dependent fashion, $Os(CO)_4(C_2H_4)$ (**1**) and $Os(CO)_3(C_2H_4)_2$ (**2**) in excellent and moderate yields, respectively[4] (eq 1).

$$\mathrm{Os(CO)_5} + \mathrm{C_2H_4(purge)} \xrightarrow[\text{butane, }-20\ ^\circ\mathrm{C}]{h\nu,\ \lambda > 370\ \mathrm{nm}} \underset{\mathbf{1}\ (92\%)}{\mathrm{Os(CO)_4(C_2H_4)}}$$

$$\mathbf{1} + \mathrm{C_2H_4(purge)} \xrightarrow[\text{pentane, }-20\ ^\circ\mathrm{C}]{h\nu,\ \lambda > 330\ \mathrm{nm}} \underset{\mathbf{2}\ (35\%)}{\mathrm{Os(CO)_3(C_2H_4)_2}} \qquad (1)$$

Further photolysis at low temperature, which is especially rapid and efficient in a quartz vessel, results in IR changes which are

---

* Address correspondence to this author.

(1) Parts of this report were first presented at the 69th Canadian Chemical Conference, Saskatoon, Saskatchewan, Canada, June 1986: Abstr. IN-DP-16.

(2) (a) King, R. B. In *The Organic Chemistry of Iron*; Koerner von Gustorf, E. A., Grevels, F.-W.; Fischler, I., Eds.; Academic: New York, 1978; Vol. 1, p 397. (b) Grevels, F.-W.; Reuvers, J. G. A.; Takats, J. *J. Am. Chem. Soc.* **1981**, *103*, 4069. (c) Fleckner, H.; Grevels, F.-W.; Hess, D. *J. Am. Chem. Soc.* **1984**, *106*, 2027. (d) Grevels, F.-W.; Reuvers, J. G. A.; Takats, J. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 452. (e) Krüger, C.; Rabe, E.; Grevels, F.-W.; Moser, R.; Ball, R. G.; Kiel, G.-Y.; Takats, J. unpublished results.

(3) Wuu, Y.-M.; Bentsen, J. G.; Brinkley, C. G.; Wrighton, M. S. *Inorg. Chem.*, in press. We thank Professor Wrighton for communicating his results prior to publication.

(4) Full characterization of compounds **1** and **2** appears in the supplementary material. Compound **1** has been described before.[5] It is interesting to note that small amounts of $Os_2(CO_8)(\mu\text{-}\eta^1,\eta^1\text{-}C_2H_4)$[6,7] ($\sim$8%) are also formed in the first step of eq 1.

(5) Carter, W. J.; Kelland, J. W.; Okrasinski, S. J.; Warner, K. E.; Norton, J. R. *Inorg. Chem.* **1982**, *21*, 3955.

(6) Motyl, K. M.; Norton, J. R.; Schauer, C. K.; Anderson, O. P. *J. Am. Chem. Soc.* **1982**, *104*, 7325.

(7) Burke, M. R.; Takats, J.; Grevels, F.-W.; Reuvers, J. G. A. *J. Am. Chem. Soc.* **1983**, *105*, 4092.

(8) **5**, colorless moderately air stable solid: IR(pentane) ν_{CO} 1939 cm^{-1}; ^{1}H NMR (CD_2Cl_2, 25 °C) δ 0.88 (d, J = 8 Hz, PMe_3), 1.69 (d, J = 8 Hz, PMe_3), 0.8 (m, 2 H), 1.2 (m, 2 H), 1.3 (m, 2 H), 1.8 (m, 2 H); ^{13}C NMR (CD_2Cl_2, −20 °C) δ 183.0 (dd, J = 7, 109 Hz, CO), 21.6 (d, J = 31 Hz, PMe_3), 11.5 (d, J = 27 Hz, PMe_3), 10.5 (d, J = 7.0 Hz, $\mathit{C}H_2CH_2$), 3.8 (d, J = 6 Hz, $CH_2\mathit{C}H_2$); ^{31}P NMR (CD_2Cl_2, 25 °C) δ −53.2 (d, J = 23 Hz), −54.2 (d, J = 23 Hz); yield, 48%.

0002-7863/87/1509-2227$01.50/0

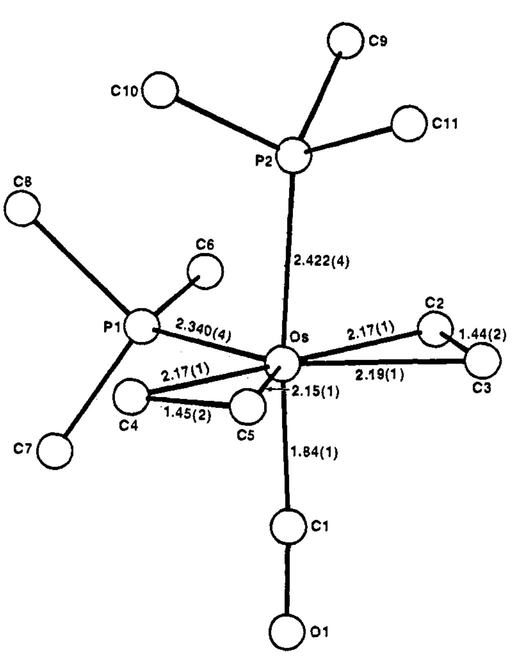


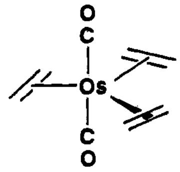
Figure 1. Prespective view of **5** with relevant bond distances.

best accommodated by the formation of $Os(CO)_2(C_2H_4)_3$ (**3**) and $Os(CO)(C_2H_4)_4$ (**4**), eq 2. Prolonged photolysis will result in

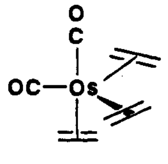
$$2 + C_2H_4(\text{purge}) \xrightarrow[\text{pentane, } -20\ ^\circ C]{h\nu,\ \lambda > 240\text{ nm}} \underset{3}{Os(CO)_2(C_2H_4)_3} + \underset{4}{Os(CO)(C_2H_4)_4} \quad (2)$$

complete conversion to **4** as evidenced by the unique CO stretching frequency at 1978 cm^{-1}, different from those of **3** (vide infra). Due to its instability, compound **4** has so far defied further characterization; however, strong indirect evidence for its correct formulation comes from the reaction with 2 equiv of PMe_3 which gives a moderately air stable colorless solid, identified as $Os(PMe_3)_2(C_2H_4)_2(CO)$ (**5**).[8] The spectral data obtained for **5** uniquely identify the coordination geometry as trigonal bipyramidal with axial and equatorial PMe_3 moieties and two equatorial ethylene ligands. The ^1H NMR features are temperature independent (−115 to +90 °C) and indicate a rigid five-coordinate geometry and, astonishingly, *no* ethylene rotation up to +90 °C. Clearly compound **5** results from the displacement of an axial and equatorial ethylene ligand from the presumably also trigonal bipyramidal **4** by trimethylphosphine. To confirm the geometry, the structure was determined by single-crystal X-ray crystallography,[9] Figure 1. It is evident that the solid-state structure corroborates the above prediction.

Even though the photolysis experiment with careful monitoring can be stopped at the tris(ethylene) stage, a more convenient synthesis of **3** involves brief carbonylation of a solution that appears to contain only **4** by IR spectroscopy. Unexpectedly, **3** exists as a mixture of two isomeric trigonal-bipyramidal forms, axial/axial-CO (**3a**) and axial/equatorial-CO (**3b**).[10] Conclusive proof was provided by the variable-temperature ^{13}C and ^1H NMR spectra. The low-temperature limiting spectra are shown in Figure 2. The ^{13}C NMR spectrum at −100 °C shows four singlets for the olefinic carbon atoms. The ethylenic carbons of **3a** are equivalent and resonate at 23.8 ppm. The observation of three singlets for **3b** in a 1:1:1 ratio indicates stoppage of rotation of the two equatorial ethylenes. Noteworthy is the large difference between the chemical shifts of the equatorial and axial ethylene moieties. The low field position of the latter indicates significantly reduced back-bonding to the axial olefinic group. In accord with this and with the nearly degenerate d orbitals for Os–axial olefin back-bonding, the axial ethylene is still rapidly rotating even at this low temperature (single peak in the ^1H NMR spectrum). As the temperature is raised the signals assigned to the equatorial ethylenes broaden, indicating onset of olefin rotation in the equatorial plane. At 0 °C all three ethylenes of **3b** have averaged



3a



3b

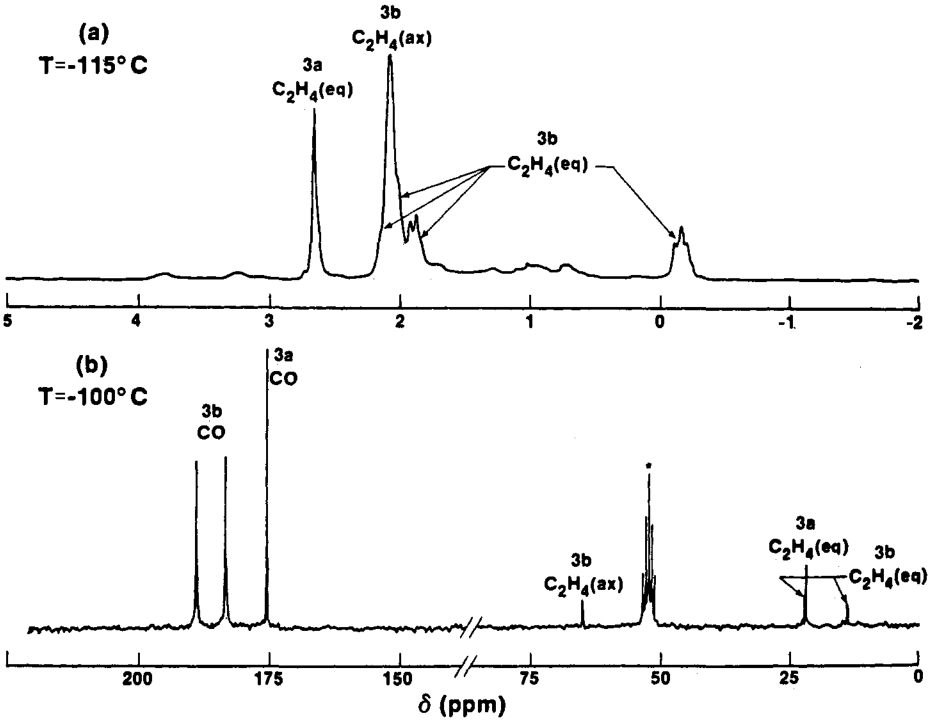


Figure 2. (a) ^1H and (b) ^{13}C NMR spectrum of **3a** and **3b** at low temperature. The ^{13}C NMR spectrum was recorded on ^{13}CO-enriched **3**.

presumably via a turnstile-type rotation. At this temperature exchange between **3a** and **3b** is still slow.

In summary, we have shown that the osmium center allows the isolation of a wide range of simple ethylene/carbonyl complexes. The scope of the ethylene displacement reaction from **3** and **4** is currently being evaluated as a means to synthesize other mononuclear osmium complexes.

Acknowledgment. We thank NSERC and MPI for financial support, Dr. R. G. Ball for structure determination, and Johnson Matthey for generous loan of OsO_4.

Supplementary Material Available: Spectroscopic data on **1** and **2** and tables of cell parameters, positional and thermal parameters, and bond distances and angles of **5** (3 pages). Ordering information is given on any current masthead page.

---

(9) The structure determination was carried out by Dr. R. Ball of the Structure Determination Laboratory of the Department of Chemistry, University of Alberta. At the present stage of refinement the agreement factors are $R = 0.055$, $R_W = 0.064$.

(10) **3a**: IR (pentane) ν_{CO} 1945 (s) cm^{-1}; ^{1}H NMR (CD_2Cl_2, −115 to 0 °C) δ 2.69 (s); ^{13}C NMR (CD_2Cl_2, −100 °C) δ 23.8 (s, C_2H_4), 175.9 (CO). **3b**: IR (pentane) ν_{CO} 2026 (s), 1982 (s) cm^{-1}; ^{1}H NMR (CD_2Cl_2, −115 °C) δ 2.12 (br with shoulders, 8 H), 1.92 (br q, 2 H), −0.15 (br t, 2 H); (0 °C) δ 1.82 (br s); ^{13}C NMR (CD_2Cl_2, −100 °C) δ 66.2 (s, C_2H_4(ax)), 23.9 and 15.8 (s, s, C_2H_4(eq)) 189.3 and 183.8 (CO).

Computer Software Reviews

ChemCad. C Graph Software, Inc. P.O. Box 5641, Austin, TX 78763. List Price $250.00 or $175.00 for academic users. If you purchase version 1.0, a second version 1.1 will be provided free when it is completed. Further updates will cost about $50.00.

ChemCad is an interactive graphics program which can be utilized to create input files for MM2 and the AMPAC suite of programs, MINDO/3, MNDO, and AM1, on a microcomputer. The ability to write Cartesian coordinate files for use with other programs is also possible. The ChemCad package includes ChemCad.exe, structure libraries, and help files, as well as MNDO and MM2 programs. The MM2 and MNDO programs are not products of C Graph. MM2 is Allinger's program adapted for IBM PC compatible microcomputers and does not contain any SCF treatment for π electrons. MNDO is a direct translation of QCPE 353 to the IBM PC.

ChemCad will run on the IBM PC or compatible equipped with a graphics card, DOS 2.0 or higher, and with 348K of memory. C Graph, however, recommends 512K of memory and the 8087 coprocessor chip. The 8087 chip is not required to run ChemCad but is required to run MM2 or MNDO. With less than 640K RAM MM2 or MNDO cannot be run with ChemCad in memory. This problem can be circumvented by using ChemCad to write an input file, then running MM2 or MNDO and reading the calculated geometry file back into ChemCad. ChemCad will also support the Microsoft mechanical mouse or the PCMOUSE optical mouse. A mouse is not required, the menu cursors can be moved with the numerical key pad, but a mouse greatly enhances operation of the software.

An outstanding feature of ChemCad is the ability to create molecules from library fragments. ChemCad has resident a 40 ring library containing both hydrocarbon and heterocyclic rings. Twenty acyclic substituents are also available as well as the ability to create your own structure library. These libraries along with the function ATTACH A SUBSTITUENT and ATTACH allow the rapid construction of complicated molecules. These attach functions automatically set the bond length of the newly created bond to the sum of the covalent radii of the attached atoms. The set parameter menu allows the user, however, to change bond lengths, bond angles, and dihedral angles in the library structures. Care must be utilized in these operations however because the reference atom must belong to a different group (defined below) than the atom or group to be moved.

Structures can also be built up piece-by-piece by choosing any one of 72 elements from a periodic table. Hydrogens can be added automatically to C, N, and O and lone pairs to N and O. The hydrogens are added to complete the normal valency of these atoms (sp^2, sp^3, or sp) at the expected bond lengths and angles. Occasionally the added hydrogens will not appear on the screen because they are hidden by the atom to which they are attached.

Increased flexibility in structure manipulation is also provided by the ability to define groups and perform group manipulations. A set of atoms defined to be in the same group can be manipulated together. The set parameter commands for example can move an entire group rather than just an atom. This allows the user to set the dihedral angle between portions of the molecule in one operation.

The viewing operations include rotation about an axis, rotation around a bond, zoom-in, zoom-out, and pan. The rotations can be done in 1, 5, 10, 45, or 90° increments either clockwise or counterclockwise. In addition a three-dimensional ball and stick drawing can be generated and plotted. An information menu can be used to determine distances in angstroms or angles in degrees in either the geometry minimized or rough structure. It appears that both bond lengths and intermolecule (through space) distances are available.

The documentation is adequate and the system is easy to learn how to use. This is a convenient and powerful addition to any molecular modeling package.

Edward L. Clennan, *University of Wyoming*

Reference Manager. Version 3.2. Research Information Systems, Inc., 1991 Village Park Way, Suite 206, Encinitas, CA 92024. List prices: RM-32000, $440.00; RM-800, $195.00; RM-75, $59.00; Capture module, $59.00; Lecture module, $39.00; Journal Formats module, $39.00 (quantity discounts available).

Reference Manager is a microcomputer based software package designed specifically for preparing scientific publications. It consists of a specialized database management program combined with a text-reformatting module that enables the scientist to store bibliographic references and later incorporate them into a manuscript for publication.

Reference Manager is available for any microcomputer using the MS/PC-DOS or CP/M operating systems and a Macintosh version will be available soon. The RM-75 and RM-800 versions are not available for CP/M based systems. The RM-75 introductory package is a demonstration system that allows the user to create multiple databases, but each database is limited to 75 references. The RM-800 package provides one 800 reference database and nine 75 reference databases and was designed for use with a floppy-based system. The RM-32000 package, which allows the user to build a main database of up to 32 000 references and nine 75 reference databases, is obviously intended for use with a 10 Mb or larger hard disk system. The capture module enables downloading of references either individually or in "batch" from MED-LINE, Paper Chase, BRS Colleague MESH, MS78, MS74, MS70, and Biosis Previews. The lecture module creates a specialized file for the storage and rapid retrieval of slides for the preparation of a lecture. The journal format module contains about 100 "ready to use" formats for biomedical journals. The MS/PC-DOS versions require 256 Kb RAM and the CP/M version (2.3) requires 64 Kb RAM. Copy protection is invoked only after 200 references have been added to the database; at this time, a signed license agreement is exchanged for a "key" disk that will "unlock" the database.

The heart of Reference Manager is the database into which are entered authors, title, journal, volume:pages, year, keywords, "reference on file", and notes. Similar entries are required for book and book chapter references. Any of these fields can subsequently be corrected and references can be sorted by author, journal, and year. In addition, references can be retrieved by author, editor, journal, keyword, reference number, words or phrases in the title or notes, or any "string" in the reference.

Reference Manager operates in conjunction with many of the most