Structure of $Os(CO)_4(C_2H_4)$, an Osmacyclopropane

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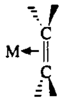
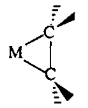
${}^1J_{^{13}C-^{13}C}$ for an ethylene coordinated to $Os(CO)_4$ has been determined as 39.0 (2) Hz from the ${}^1H$ NMR spectrum of $Os(CO)_4(\eta^2-{}^{13}C_2H_4)$. The molecular structure of $Os(CO)_4(\eta^2-C_2H_4)$ (1) has been determined by single-crystal X-ray diffraction; 1 crystallizes in space group $C2/c$ with $a = 12.271$ (5) Å, $b = 6.778$ (1) Å, $c = 12.345$ (4) Å, $\beta = 129.49$ (2)°, $V = 792.4$ (2) Å^3, and $Z = 4$. The geometry of 1 is approximately trigonal bipyramidal, with the ethylene carbons twisted out of the equatorial plane by 4.0°. The axial carbonyls of 1 tilt *toward* the coordinated ethylene, with a C1–Os–C1′ angle of 171.3 (5)°. The optimal geometries of $Os(CO)_4$, $H_2Os(CO)_4$, and 1 have been calculated by Hartree–Fock methods. The orbital amplitude contour diagrams of a GVB(6/12) wave function for 1 show that the axial bending occurs in order to mix in virtual p_π character and improve back-bonding to the equatorial carbonyls; they also show that 1 is best described as a metallacyclopropane.

Introduction

Our current understanding of the way in which olefins are bound to transition metals[1] rests on a scheme first proposed by Dewar in 1950[2] and applied to $K[PtCl_3(C_2H_4)]$ by Chatt and Duncanson in 1953.[3] The metal behaves as both an electron acceptor (from the filled orbital associated with the olefinic π bond) and an electron donor (into the empty olefinic π^* orbital) in a π complex such as I.



π-complex
I



metallacyclopropane
II

Dewar[2] viewed a π complex (I) as becoming a metallacyclopropane (II)[4] if the forward donation from the olefin were sufficiently balanced by "back-bonding" in the reverse direction. Hoffmann and co-workers have noted that the π complex (I) and metallacyclopropane (II) pictures are equivalent, within a delocalized bonding scheme: the in- and out-of-phase combinations of the M–C σ bond orbitals in II have the same symmetries as the acceptor and donor orbitals of the metal in I.[5]

Of course I and II are distinguishable if a valence bond picture is employed; they are simply limiting resonance structures![6] Steigerwald and Goddard[7] have used generalized valence bond (GVB) wave functions to compare the energy and geometry of $Cl_2Ti(\eta^2-C_2H_4)$ in the π complex limit with its energy and geometry in the metallacyclopropane limit; by constructing limiting perfect pairing generalized valence bond representations for each limit, they have found that the energy of the metallacyclopropane is lower. They have emphasized that the two different valence bond descriptions (I and II) imply different *reactivities* and have pointed to the ability of $Cp^*{}_2Ti(C_2H_4)$[8] to insert ethylene as evidence that it is better described by an electronic structure of type II.

Our curiosity about the way the ethylene ligand is bound in the simple mononuclear complex $Os(CO)_4(C_2H_4)$ (1) was aroused by what we learned[9] about the bonding of the ethylene in $(\mu-\eta^1,\eta^1-C_2H_4)Os_2(CO)_8$ (2). Complex 2 proved to be a true dimetallacyclobutane; i.e., the carbons in its ethylene ligand are completely rehybridized to sp^3. We wondered how closely its mononuclear analogue 1 would approach being a metallacyclopropane (an ethylene complex of type II). We also needed other structural data about 1, in particular its ethylenic C–C distance, as a reference point for the solution structure determinations we have carried out on 1 and 2 in nematic phase solvents by ${}^1H$ and ${}^{13}C$ NMR.[10] Finally, we needed ${}^1J_{^{13}C-^{13}C}$ for 1 in order to assess how well this parameter indicated metallacyclopropane character.

We have therefore carried out ab initio calculations on 1, ascertained its structure by X-ray diffraction, and determined ${}^1J_{^{13}C-^{13}C}$ for its ethylene ligand.

Experimental Section

$(\eta^2-C_2H_4)Os(CO)_4$ (1)[11-14] was prepared from $Os_3(CO)_{12}$ by a

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[1] For a review, see: Mingos, D. M. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 3, Chapter 19, p 47.

[2] Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C71. This paper is actually Dewar's contribution to a colloquium held in the spring of 1950 in Montpellier, France. For an account of the evolution of π-complex theory and a general discussion of the relationship between π complexes and three-membered rings, see: Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1979**, *101*, 783.

[3] Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939.

[4] The first proposal that an olefin complex could be described as metallacyclopropane was by: Gelman, A. *C. R. Acad. Sci. URSS* **1939**, *24*, 549. However, it is now clear (Chang, T.-H.; Zink, J. I. *J. Am. Chem. Soc.* **1984**, *106*, 287) that the bonding in the complex ($K[PtCl_3(C_2H_4)]$) for which this proposal was made does not contain a large contribution from a metallacyclopropane resonance structure.

[5] Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801.

[6] Although textbooks of organic chemistry state that "Resonance structures may be defined as alternative representations of the electronic configuration of a fixed set of nuclei" (Streitwieser, A., Jr.; Heathcock, C. H. *Introduction to Organic Chemistry*, 3rd ed.; Macmillan: New York, 1981; p 11), the classical account of Pauling (Pauling, L. *Nature of the Chemical Bond*, 3rd ed.; Cornell: Ithaca, 1960; Chapter 6) clearly thinks of different resonance structures (and the corresponding wave functions) as possessing different bond lengths and angles. Thus the π-complex resonance structure I has different C–C distances, H–C–H angles, etc., than the metallacyclopropane resonance structure II.

[7] Steigerwald, M. L.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1985**, *107*, 5027. The one-electron orbitals shown in this reference for the Ti–C bond pair (their Figure 1) are quite similar to the ones we have obtained for the Os–C bond pair (Figure 3b in the present paper).

[8] Cohen, S. A.; Auburn, P. R.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 1136.

[9] (a) Bender, B. R.; Bertoncello, R.; Burke, M. R.; Casarin, M.; Granozzi, G.; Norton, J. R.; Takats, J. *Organometallics* **1989**, *8*, 1777. (b) Anderson, O. P.; Bender, B. R.; Norton, J. R.; Larson, A. P.; Vergamini, P. J. *Organometallics* **1991**, *10*, 3145.

[10] Bender, B. R.; Hembre, R. T.; Norton, J. R. Manuscript in preparation.

[11] (a) Carter, W. J.; Kelland, J. W.; Okrasinski, S. J.; Warner, K. E.; Norton, J. R. *Inorg. Chem.* **1982**, *21*, 3955. (b) Lindner, E.; Jansen, R.-M.; Hiller, W.; Fawzi, R. *Chem. Ber.* **1989**, *122*, 1403. We believe the ${}^1H$ chemical shift of 1 in C_6D_6 given in this paper (δ 0.44) to be a typographical error and the correct value in that solvent to be δ 1.44.[11a]

[12] (a) Burke, M. R.; Takats, J.; Grevels, F.-W.; Reuvers, J. G. A. *J. Am. Chem. Soc.* **1983**, *105*, 4092. (b) Burke, M. R. Ph.D. Thesis, University of Alberta, Feb 1987. (c) Takats, J. *Polyhedron* **1988**, *7*, 931.

[13] Poë, A. J.; Sekhar, C. V. *J. Am. Chem. Soc.* **1986**, *108*, 3673.

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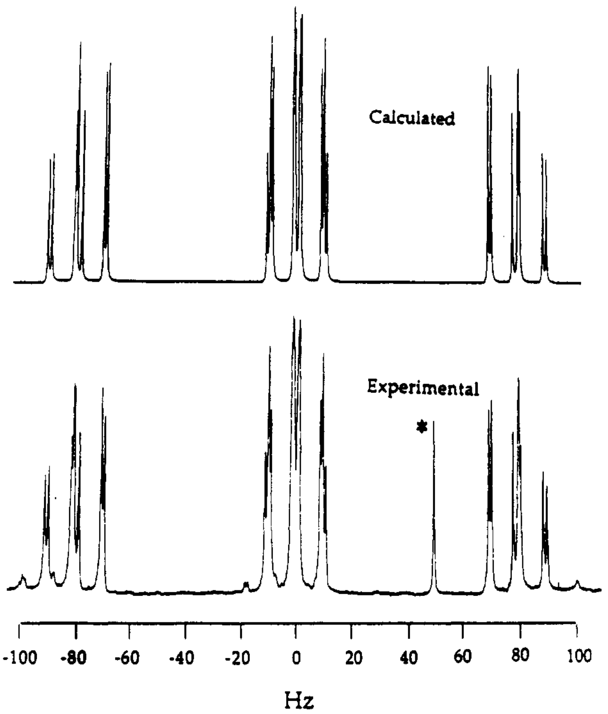

Figure 1. Experimental and calculated 200-MHz ^1H NMR spectra of 1-^{13}C in CD_2Cl_2. The peak marked with an asterisk is due to an impurity.

procedure based on that of Burke and Takats[12] and that of Poë and Sekhar[13] and described elsewhere.[9b] A Chromatotron, with pentane as eluant, was used to separate the 1 from the 2 also formed in this reaction; the resulting pentane solutions showed only the three ν(CO) bands (2109 (w), 2021 (s), and 1989 (s) cm^{-1}) characteristic of 1.[11] UV of 1 (pentane) λ_{max} 256.7, 213.4 nm. The 256.7-nm peak is accompanied by a vibrational progression (251.0, 244.2, 238.5, 233.9, and 229.3 nm; average spacing 920 cm^{-1}) which is well-resolved at room temperature; it is probably an Os → C_2H_4 charge-transfer band with the vibrational progression being ν(CC) of its excited state.

Solvent-free 1 was obtained by high-vacuum fractionation. After freeze–pump–thaw degassing, the pentane solution containing 1 was fractionated under dynamic vacuum (10^{-4} mmHg) by slowly passing it through two U-traps in series, the first of which was surrounded by a CH_3CN/liquid N_2 slush bath (−40 °C) and the second of which was surrounded by liquid N_2 only (−197 °C). Pure 1 condensed in the −40 °C U-trap as clear, colorless crystals, mp −14 °C.[11b] Yield 79 mg, 0.24 mmol, 72%; ^1H NMR of 1 (CD_2Cl_2) δ 1.77 (s). Neat 1 is stable indefinitely when stored in a −20 °C freezer but yellows upon standing at room temperature.

1-^{13}C and 1-$^{13}C_2$ were prepared by a modification of the procedure for 1. For 1-^{13}C, $Os_3(CO)_{12}$ (100 mg, 0.110 mmol) was placed in a 30-mL standard vacuum bulb that contained a stir bar, and ~25 mL of CH_2Cl_2 (distilled from P_4O_{10}) was vacuum transferred into it and thoroughly degassed. $^{13}CH_2CH_2$ (218 mL at 55 Torr, 0.64 mmol) was then vacuum transferred into the bulb. After thawing, the mixture was photolyzed for 96 h with λ > 436 nm light to give a clear, colorless solution. The unused $^{13}CH_2CH_2$, solvent, 1-^{13}C, and 2-^{13}C were then separated by high-vacuum fractionation: the mixture was distilled from a hexane/liquid N_2 (−94 °C) slush bath through a U-tube in an *n*-pentane/liquid N_2 (−131 °C) slush bath followed by a U-tube cooled by liquid N_2. Only $^{13}CH_2CH_2$ collected in the liquid N_2 trap (by gas-phase IR), whereas much of the solvent condensed in the −131 °C trap. The mixture of solvent, 1-^{13}C, and 2-^{13}C remaining in the reaction bulb was separated by a second vacuum fractionation using an ice bath, a CH_3CN/liquid N_2 (−40 °C) slush bath, and liquid N_2; 1-^{13}C was collected in the −40 °C trap and then vacuum transferred into a tared bulb (yield 21.8 mg, 0.066 mmol, 60%). Its solution IR spectrum (ν(CO) region) was identical to that of the unlabeled complex. The ^1H NMR (200 MHz, CD_2Cl_2) of 1-^{13}C is shown in Figure 1.

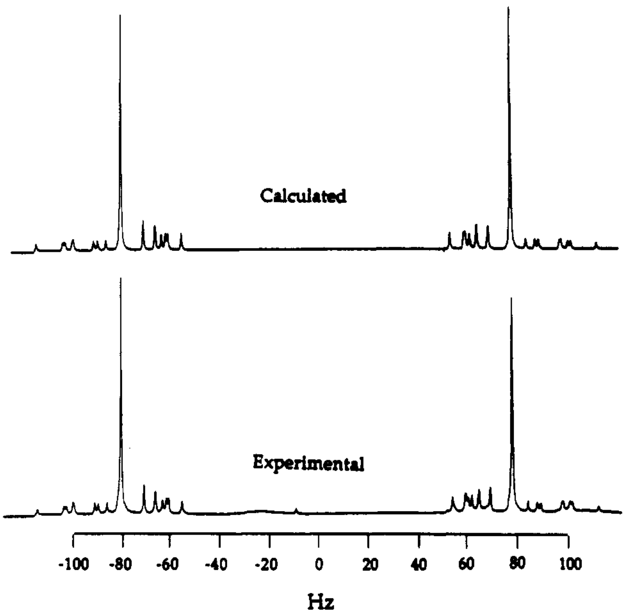

Figure 2. Experimental and calculated 200-MHz ^1H NMR spectra of 1-$^{13}C_2$ in CD_2Cl_2.

For 1-$^{13}C_2$, $Os_3(CO)_{12}$ (74.6 mg, 0.082 mmol) was photolyzed for 36 h in the presence of $^{13}C_2H_4$ (275 Torr, 110.6 mL, 0.164 mmol). The same separation procedure gave 1-$^{13}C_2$ (yield 22 mg, 0.066 mmol, 81%). Its solution IR spectrum (ν(CO) region) was identical to that of the unlabeled complex. The ^1H NMR (200 MHz, CD_2Cl_2) of 1-$^{13}C_2$ is shown in Figure 2.

(η^2-CH_2CHCH_3)Os(CO)$_4$ (3)[11b] was prepared by the same general method as 1. The output of a high-pressure 450-W Hanovia lamp was passed through a saturated aqueous solution of $NaNO_2$ so that only light with λ > 436 nm remained. A suspension of $Os_3(CO)_{12}$ (300 mg) in 250 mL of CH_2Cl_2 was equilibrated with 20 psig propylene in a 500-mL Fischer–Porter apparatus and kept under that olefin pressure while being irradiated for 12 h. The separation and isolation of 3 were performed as quickly as possible due to the instability of its dinuclear analogue toward propylene dissociation ($t_{1/2}$ ~ 2.2 h at 25 °C). The solvent was removed under reduced pressure after the Fischer–Porter apparatus was vented, and 3 was separated from (μ-CH_2CHCH_3)$Os_2(CO)_8$[15] on a Chromatotron as described above for 1 and 2; the first band contained 3. Samples of 3, which is less stable than its ethylene analogue, 1, were isolated in 75% yield by low-temperature vacuum fractionation as described above for 1. Spectroscopic data for 3: IR (pentane) 2105 (w), 2016 (vs), 1986 (s) cm^{-1}, in agreement with that reported;[11b] ^1H NMR (200 MHz, CD_2Cl_2) δ 1.81 (dd, 1 H, $^2J_{gem}$ = −2.6 Hz, $^3J_{trans}$ = +11.0 Hz), 2.04 (d, 3 H, $^3J_{HH}$ = +6.1 Hz), 2.15 (dd, 1 H, $^2J_{gem}$ = −2.6 Hz, $^3J_{cis}$ = +8.3 Hz), 2.78 (m, 1 H, $^3J_{cis}$ = +8.3 Hz, $^3J_{trans}$ = +11.0 Hz, $^3J_{HH}$ = +6.1 Hz).

(η^2-*trans*-$CH_3CHCHCH_3$)Os(CO)$_4$ (4a) and (η^2-$CH_3CHCHCH_3$)Os(CO)$_4$ (4b). When a suspension of $Os_3(CO)_{12}$ was irradiated in the presence of *trans*-2-butene under the conditions used for ethylene and propylene, a precipitate began to form before its yellow color disappeared. If the photolysis was stopped after several hours, both **4a** and the $Os_2(CO)_8$ adduct of *trans*-2-butene were present and could be separated and isolated in low yields (<25%) by the procedures described above. With *cis*-2-butene under the same conditions, a similar precipitate was observed, but only **4b** could be isolated in low yield if the photoreaction was stopped after several hours. No *trans*-2-butene adducts were isolated from reactions with *cis*-2-butene and no *cis*-2-butene adducts were isolated from reactions with *trans*-2-butene.

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(15) Haynes, A.; Poliakoff, M.; Turner, J. J.; Bender, B. R.; Norton, J. R. *J. Organomet. Chem.* **1990**, *383*, 497.

Table I. *J* Coupling Constants[a] for $^{13}C_2H_4$, $(^{13}CH_2{}^{12}CH_2)Os(CO)_4$ (1-^{13}C), and $(^{13}C_2H_4)Os(CO)_4$ (1-$^{13}C_2$)

	J (Hz)		
pair	$^{13}C_2H_4$	$(^{13}CH_2{}^{12}CH_2)Os(CO)_4$	$(^{13}C_2H_4)$-$Os(CO)_4$
$^2J_{gem}$	+2.5 (2)	−9.8 (2)	−9.9 (2)
$^3J_{cis}$	+11.1 (1)	+9.0 (2)	+9.0 (2)
$^3J_{trans}$	+19.1 (1)	+11.1 (2)	+11.2 (2)
$^1J_{CH}$	+156.4 (2)	+158.1 (2)	+158.1 (2)
$^2J_{CH}$	−2.4 (2)	+0.3 (2)	+0.3 (2)
$^1J_{CC}$	+67.6 (1)		+39.0 (2)

[a] The relative signs of all coupling constants have been determined by spectrum simulation; the absolute signs given are based on the assumption that $^1J_{CH}$ is positive.

Spectroscopic data for **4a**: IR (pentane) 2105 (w), 2013 (vs), 1982 (m, br) cm^{-1}; ^{1}H NMR (200 MHz, CD_2Cl_2) δ 2.77 (m, 2 H), 2.02 (m, 6 H), $^3J_{trans}$ = +10.5 (2) Hz, $^3J_{H-CH_3}$ = +6.5 (2) Hz. Spectroscopic data for **4b**: IR (pentane) 2105 (w), 2017 (vs), 1987 (m, br) cm^{-1}; ^{1}H NMR (200 MHz, CD_2Cl_2) δ 3.16 (m, 2 H), 2.08 (m, 6 H), $^3J_{cis}$ = +9.1 (2) Hz, $^3J_{H-CH_3}$ = +6.5 (2) Hz.

Analysis of ^{1}H NMR Spectra. All five of the *J* coupling constants for the AA′A″A‴X spin system[16] in 1-^{13}C were extracted from its ^{1}H spectrum by trial and error simulation with PANIC.[17] The calculated spectrum is shown along with the experimental one in Figure 1, and the coupling constants have been placed in Table I along with the corresponding coupling constants for free $^{13}CH_2CH_2$ determined by Lynden-Bell and Sheppard.[18]

The same five coupling constants as well as $^1J_{CC}$ were extracted from the ^{1}H NMR spectrum of 1-$^{13}C_2$ (an AA′A″A‴XX′ spin system[16]). The calculated spectrum is shown along with the experimental one in Figure 2, and the coupling constants thereby obtained have also been placed in Table I.

Crystal Mounting. Single crystals of 1 can be grown, selected, and mounted despite the fact that it has a melting point of −14 °C[11b] and is soluble in all common organic solvents. A concentrated solution (75–100 mg of 1 in 1–2 mL of pentane) was placed in a high-vacuum bulb. When this solution formed no crystals overnight in a −20 °C freezer, the bulb was immersed in a low-temperature bath and cooled to −80 °C over a period of 2 days. Well-formed crystals of 1 were then apparent. The bulb was quickly transferred to a −78 °C dewar and the pentane solvent removed under high vacuum for several hours.

The cold stage plate used in the selection of crystals of 1 has been described in detail.[19] It allowed crystals of 1 to be examined and selected at −78 °C under a blanket of cold argon. The tip of the goniometer pin was dipped in vacuum grease and chilled; a suitable crystal of 1 was then selected and stuck to that tip. The goniometer pin with the mounted crystal was *quickly* transferred to the goniometer, mounted in a stream of cold N_2 vapor, and maintained at −130 °C throughout the X-ray diffraction equipment.

Crystallographic Study of 1. Crystal size 0.24 × 0.29 × 0.41 mm; $C_6H_4O_4Os$, fw 330.3; monoclinic, space group $C2/c$, a = 12.271 (5) Å, b = 6.778 (1) Å, c = 12.345 (4) Å, β = 129.49 (2)°, V = 792.4 (2) Å^3; Z = 4, D_x = 2.77 g cm^{-3}; λ(Mo Kα) = 0.7107 Å; μ = 160.8 cm^{-1}; T = −130 °C; $F(000)$ = 592; Siemens $R3m$ diffractometer; unit cell constants from least squares fit of settling angles for 25 reflections ($2\theta_{av}$ = 24.47°). Data collected ($\theta/2\theta$ scans) to $(\sin\theta)/\lambda$ = 0.5947 Å^{-1}, $-15 \le h \le +15$, $0 \le k \le +9$, $0 \le l \le +15$. Three standard reflections (200, 020, 002) every 97; Lorentz and polarization corrections; empirical absorption correction based on intensity profiles for selected reflections obtained by rotation about the diffraction vector (T_{min} = 0.125, T_{max} = 0.230, R_{merge} = 0.10 (before) and 0.06 (after)); 705 unique reflections, 701 reflections with $F_o > 2.5\sigma(F_o)$ observed.

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for 1[a]

	x	y	z	U
Os	0	5581 (1)	7500	15 (1)*
O1	−2864 (9)	6101 (15)	6834 (9)	35 (5)*
O2	1185 (9)	2883 (12)	10021 (8)	36 (4)*
C1	−1814 (13)	5797 (13)	7079 (12)	19 (6)*
C2	758 (11)	3877 (17)	9077 (11)	24 (5)*
C3	−415 (11)	8668 (14)	6726 (11)	28 (6)*

[a] Entries marked with an asterisk correspond to an equivalent isotropic U defined as one-third of the trace of the orthoganolized U_{ij} tensor.

Table III. Carbon and Oxygen Gaussian Basis Sets

	shell	ζ	coefficient
carbon	S	5.020	−0.304 1326
	S	0.5285	1.099 2272
	S	0.1632	1.0
	P	9.558	0.056 7759
	P	2.021	0.311 8989
	P	0.5500	0.761 7496
	P	0.1524	1.0
oxygen	S	9.750	−0.311 5558
	S	1.051	1.102 9867
	S	0.3135	1.0
	P	17.76	0.063 2162
	P	3.866	0.333 4906
	P	1.050	0.741 0064
	P	0.2764	1.0

The structure was solved by Patterson map interpretation and refined by full matrix (51 parameters total, data/parameters = 13.7) weighted [$w = (\sigma^2(F) + gF^2)^{-1}$, $g = 3 \times 10^{-4}$] least-squares refinement on F. H atoms were placed in idealized positions (C–H = 0.96 Å, U(H) = 1.2 × U_{iso}(C)). Non-H atoms were refined with anisotropic thermal parameters. At convergence ($(\Delta/\sigma)_{max}$ = 0.003, $(\Delta/\sigma)_{mean}$ = 0.002 for the last cycle) R = 0.041, R_w = 0.052, S = 2.6, the slope of the normal probability plot = 2.5, $(\Delta\rho)_{max}$ = +2.3 e Å^{-3} (0.9 Å from Os), and $(\Delta\rho)_{min}$ = −2.5 e Å^{-3}. Neutral atom scattering factors and anomalous dispersion corrections were used;[20] all calculations were performed using the SHELXTL program library.[21] Crystallographic data other than the final atomic coordinates and thermal parameters (Table II) appear as supplementary material (anisotropic thermal parameters and H coordinates) or can be obtained from the author (structure factors).

Calculational Details. All of the calculations reported here were carried out using Cartesian Gaussian basis sets. For carbon and oxygen the effective core potentials of Stevens and Krauss[22] were used to replace the 1s electrons, allowing self-consistent orbital optimization to be carried out only for the valence electrons. For Os, the Hay and Wadt[23] effective potential was used to replace the core orbitals up through n = 4, again reducing the number of functions for the self-consistent orbital optimization. A scaled basis was used for the hydrogens.[24] The basis as given by Hay and Wadt[23] was used for osmium. For carbon and oxygen the valence double ζ basis listed in Table III was used. The geometries for $Os(CO)_4$, $Os(CO)_4H_2$, and $Os(CO)_4(C_2H_4)$ (1) were generated with analytic gradient techniques using a restricted Hartree–Fock wave function and Newton–Raphson steps,[25] with the restriction of C_{2v} symmetry. The second derivatives used were estimated using Badger's rules[26] and updated with finite differences of the

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(16) Hoffman, R. A.; Forsén, S.; Gestblom, B. In *NMR Basic Principles and Progress*; Diehl, P.; Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin, 1969; Vol. 5.

(17) A computer program provided by IBM Instruments, Inc., known as Parameter Adjustment in NMR by Iteration Calculation (PANIC), was used for simulation of spectra and refinement of parameters on an Aspect 2000 computer.

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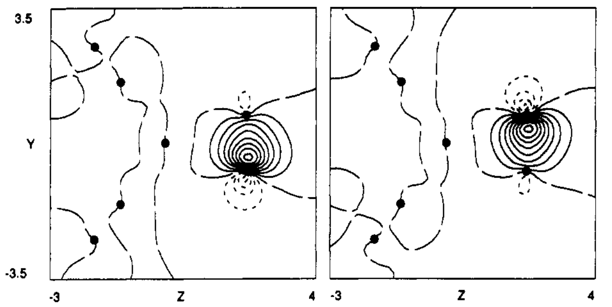
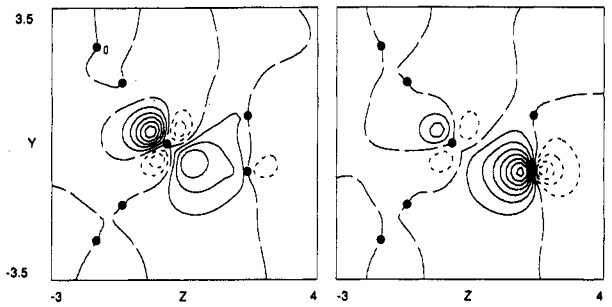
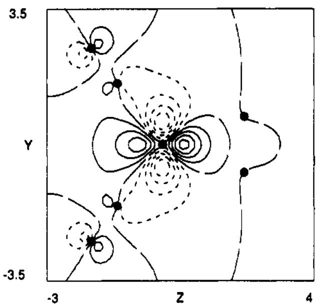
a) C-C σ Bond Pair



b) Os-C σ Bond Pair



c) Os dz2-y2



d) Os d π

e) Os d π distorted

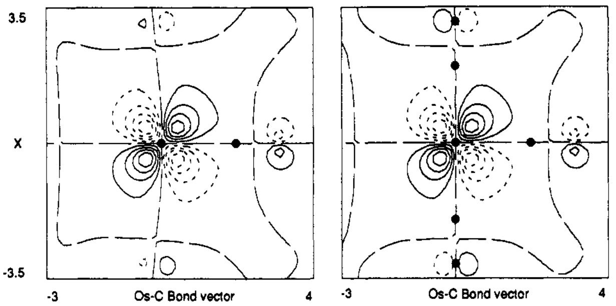


Figure 3. Contour plots of the orbitals defining (a) the GVB one-electron orbitals of the C–C σ bond (b) the GVB one-electron orbitals of one of the two Os–C σ bonds, (c) the remaining equatorial d orbital, (d) one of the d_π lone pairs for the optimized structure, and (e) the same d_π lone pair for a forced axial structure. The plotting plane for a–c contains Os, the two carbons of the ethylene, and the two equatorial carbonyl ligands. The plotting plane for d passes through Os and the C of one of the two equatorial carbonyls, is perpendicular to the equatorial plane, and nearly passes through the axial carbonyl ligands. The plotting plane for e is the same as for d, but it now contains the axial carbonyl ligands. The solid contours define positive orbital amplitude (spaced 0.0625 au), the dashed contours define negative orbital amplitude, and the long dashed lines define nodal lines.

gradient at each geometry using a procedure implemented by Upton and Rappé.[27] At the final optimized geometry a GVB-(6/12) wave function[28] was obtained for 1; the contour plots are shown in Figure 3.

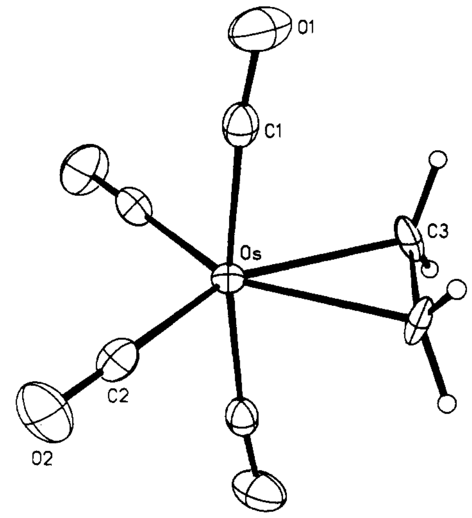


Figure 4. Structure of 1.

Table IV. Bond Lengths and Angles for 1

	Bond Lengths (Å)		
Os–C1	1.943 (17)	Os–C2	1.920 (12)
Os–C3	2.221 (10)	O1–C1	1.139 (20)
O2–C2	1.145 (15)	C3–C3A	1.488 (24)
	Bond Angles (deg)		
C1–Os–C2	92.9 (6)	C1–Os–C3	84.5 (5)
C2–Os–C3	146.5 (5)	C1–Os–C1A	171.3 (5)
C2–Os–C1A	92.3 (5)	C2–Os–C2A	106.0 (7)
C3–Os–C2A	107.4 (5)	C1–Os–C3A	87.4 (5)
C3–Os–C3A	39.2 (6)	Os–C1–O1	173.9 (9)
Os–C2–O2	178.2 (14)	Os–C3–C3A	70.4 (3)

Results

$^1J_{^{13}C-^{13}C}$ and Other Scalar Coupling Constants of the Ethylene Ligand of 1. The inclusion of one ^{13}C nucleus, as in $(\eta^2\text{-}^{13}CH_2{}^{12}CH_2)Os(CO)_4$ (1-^{13}C), transforms the A_4 spin system of 1 into an AA′A″A‴X one.[16] The inclusion of two ^{13}C nuclei, as in $(\eta^2\text{-}^{13}C_2H_4)Os(CO)_4$ (1-$^{13}C_2$), transforms the spin system into an AA′A″A‴XX′ one[16] and allows $^1J_{^{13}C-^{13}C}$ to be determined.

The coupling constants in Table I determined from the ^1H NMR spectra of 1-^{13}C agree well with those determined from the ^1H NMR spectra of 1-$^{13}C_2$. The assignment of the larger ^3J (11.1 Hz) for 1 as $^3J_{trans}$ and the smaller ^3J (9.0 Hz) as $^3J_{cis}$ is supported by comparison with the corresponding coupling constants in **3**, **4a**, and **4b**. The *trans*-2-butene Os(CO)$_4$ adduct **4a** has ^3J (which must be $^3J_{trans}$) = 10.8 (5) Hz, while the *cis*-2-butene adduct **4b** has ^3J (which must be $^3J_{cis}$) = 9.1 (1) Hz. The propylene adduct **3** has two coupling constants, 11.1 (2) and 8.3 (2) Hz, which can be assigned as $^3J_{trans}$ and $^3J_{cis}$ by comparison with the values in **4a** and **4b**; this assignment for **3** is consistent with the J values assigned for the Fe(CO)$_4$ propene adduct.[29] The assignments in Table I thus give $^3J_{trans}$ and $^3J_{cis}$ consistent values throughout this series of compounds.

Structure of 1 As Determined by X-ray Diffraction. The results of the X-ray study of 1 (final atomic coordi-

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(26) Badger, R. M. *J. Chem. Phys.* **1934**, *2*, 128; **1935**, *3*, 710.

(27) Rappé, A. K.; Upton, T. H. *Organometallics* **1984**, *3*, 1440. Upton, T. H.; Rappé, A. K. *J. Am. Chem. Soc.* **1985**, *107*, 1206.

(28) Bobrowicz, F. W.; Goddard, W. A. In *Modern Theoretical Chemistry: Methods of Electronic Structure Theory*; Schaefer, H. F., III, Ed.; Plenum: New York, 1977; Vol. 3, Chapter 4, pp 79–127.

(29) Kane, V. V.; Light, J. R. C.; Whiting, M. C. *Polyhedron* **1985**, *4*, 533.

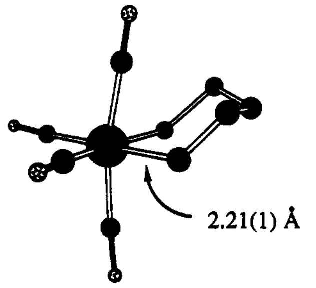

Figure 5. Structure of the osmacylohexane 6 (carbon = striped circles, oxygen = dotted circles) from ref 11b. The hydrogen atoms have been omitted for clarity.

nates and equivalent isotropic thermal parameters for non-hydrogen atoms) are given in Table II, and the structure is illustrated in Figure 4. The bond lengths and angles calculated from the coordinates in Table II are given in Table IV.

The geometry of 1 is approximately the one expected from the familiar structure of (alkene)$Fe(CO)_4$ complexes[30-33] and of the bis(trimethylsilyl)acetylene complex (η^2-$Me_3SiC_2SiMe_3$)$Os(CO)_4$ (5);[34] this geometry is traditionally called "trigonal bipyramidal",[31] with the olefin or acetylene considered as replacing one of the equatorial carbonyl ligands in $M(CO)_5$.[35] However, the site symmetry imposed on the molecules of 1 by the crystal lattice (the osmium atom lies in a special position of the *C*2/*c* space group) is C_2 rather than C_{2v}. The ethylene carbon atoms C3 and C3′ are thus not crystallography required to lie in the "equatorial plane" containing the carbonyl carbons C2 and C2′. Indeed, the Os–C3–C3′ plane of 1 is tilted by 4.0° relative to the Os–C2–C2′ plane, a tilt somewhat larger than that (1.5°) observed[34] in the related bis(trimethylsilyl)acetylene complex 5.

It is worth considering whether the detailed structure of 1 is quantitatively closer to that expected for a π complex (valence bond structure I in the Introduction) or that expected for an osmacyclopropane (valence bond structure II in the Introduction). We must ask whether the methylene ligands in 1 can be viewed as alkyl ligands connected by a C–C single bond. The large uncertainty in the C–C bond length of 1 (1.488 (24) Å) makes it difficult to compare the value of this parameter in 1 with the values reported for other ethylene complexes. The Os–C bond length in 1 (2.22 (1) Å offers a better argument for classifying it as an osmacyclopropane: this bond length is equivalent to the lengths (2.201 (9) and 2.21 (1) Å) of the Os–C single bonds in the osmacyclohexane (6) shown in Figure 5[11b] and to the lengths (2.217 (2) and 2.224 (2) Å) of the Os–C single bonds in the diosmacyclobutane 2.[9b]

Table V. Theoretically Determined Geometric Parameters[a]

parameter	$Os(CO)_4$	$H_2Os(CO)_4$	$Os(CO)_4(C_2H_4)$ (1)
$Os–C_a$	1.996	1.979	1.986
$Os–C_e$	1.948	2.010	1.970
Os–H		1.676	
$Os–C_o$			2.249
$C_o–C_o$			1.437
$C_o–H$			1.074
$C_a–Os–C_a$	170.52	160.66	172.00
$C_e–Os–C_e$	135.30	99.97	106.52
$Os–C_a–O_a$	177.63	174.41	177.20
$Os–C_e–O_e$	170.05	177.85	179.67
H–Os–H		85.10	
$C_o–Os–C_o$			37.25
$H–C_o–H$			112.70

[a] Distances are given in angstroms and angles in degrees.

The bonds between the osmium of 1 and its equatorial carbonyls C2 and C2′ (1.920 (12) Å) do not differ significantly in length from the bonds between the osmium and the axial carbonyls C1 and C1′ (1.942 (17) Å). The angle between the equatorial carbonyls (C2–Os–C2′) is only 106.0 (7)°, significantly smaller than the 120° characteristic of a trigonal bipyramid. (The C_{eq}–Os–C_{eq} angle in osmacyclohexane 6, with its larger ring, is 94.3 (4)°.[11b])

An unexpected result clearly evident in the structure of 1 in Figure 4 is the bending of the axial CO ligands *toward* the coordinated ethylene, with a C1–Os–C1′ angle of 171.3 (5)°. Similar bending can be found in the published structures of other $Os(CO)_4$ complexes: the axial carbonyls bend toward the bis(trimethylsilyl)acetylene ligand in 5 with a C–Os–C angle of 171.6 (3)°,[34] toward the ring carbons in osmacyclohexane 6 (see Figure 5) with an angle of 167.4 (4)°,[11b] toward the ring carbon and the other osmium in diosmacyclobutane 2 with an angle of 168.9°,[9b] toward the hydride ligands in $H_2Os(CO)_4$ with an angle of 161.3° (found in an unpublished electron diffraction study[36]), and toward the (phosphine)gold ligands in $(Ph_3PAu)_2Os(CO)_4$ with an angle of 157.4°.[37] Such bending has even been observed for the monohydride complexes $HMn(CO)_5$, $H_2Fe(CO)_4$, and $HCo(CO)_4$ in electron diffraction studies.[38]

Ball, Burke, and Takats have called attention[34] to the axial carbonyl bending in 5 and have suggested that donation by the $\pi_\perp$ MO of the coordinated alkyne is at least partly responsible. The X-ray results for 1, however, show the axial carbonyls in an $Os(CO)_4L$ complex bending toward the equatorial ligand even when L ($=C_2H_4$) is *not* a π donor. We have therefore used ab initio structural calculations to explore the reasons such axial carbonyl bending occurs.

Structural Results from ab Initio Electronic Structure Calculations. The results of Hartree–Fock geometry optimization for $Os(CO)_4$, $H_2Os(CO)_4$, and 1, with the assumption of C_{2v} symmetry, are collected in Table V. The geometry calculated for 1 is, as expected, approximately trigonal bipyramidal. The calculated bond lengths and angles agree well with the X-ray results in Table IV, although the agreement is in general better for angles than for bond lengths.

The calculated C–C distance of 1.44 Å is on the short side of the substantial range implied by the X-ray result in Table IV (1.488 (24) Å).[39,40] The calculated Os–C-

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(30) (a) Electron diffraction determination of the structure of $(C_2H_4)Fe(CO)_4$: Davis, M. I.; Speed, C. S. *J. Organomet. Chem.* 1970, *21*, 401. (b) Electron diffraction determination of the structure of (C_2F_4)-$Fe(CO)_4$: Beagley, B.; Schmidling, D. G.; Cruickshank, D. W. J. *Acta Crystallogr.* 1973, *B29*, 1499.

(31) Early X-ray determinations of the structures of (alkene)$Fe(CO)_4$ complexes have been listed: Lei, P.; Vogel, P. *Organometallics* 1986, *5*, 2500, refs 2–14. IR and NMR studies consistent with a "trigonal bipyramidal" geometry for molecules of this type are also listed therein, in refs 15 and 16.

(32) X-ray structure of $(C_2H_4)Fe(CO)_3PMe_3$: Lindner, E.; Schauss, E.; Hiller, W.; Fawzi, R. *Angew. Chem., Int. Ed. Engl.* 1984, *23*, 711.

(33) X-ray structures of the $Fe(CO)_4$ adducts of maleic and fumaric acids: *Acta Crystallogr.* 1989, *C45*, 721.

(34) Ball, R. G.; Burke, M. R.; Takats, J. *Organometallics* 1987, *6*, 1918.

(35) An electron diffraction study of the trigonal bipyramidal $Os(CO)_5$ has recently been published: Huang, J.; Hedberg, K.; Pomeroy, R. K. *Organometallics* 1988, *7*, 2049. The common use of "trigonal bipyramidal" to describe the general features of the *geometry* of (alkyne)$M(CO)_4$ and (alkene)$M(CO)_4$ complexes should not be confused with the question of whether valence bond structure I or II is more important in the *bonding* in such complexes.

(36) Hedberg, K.; Robiette, A. G. Unpublished results.

(37) Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Sanders, A. *J. Organomet. Chem.* 1984, *260*, C29. The angle quoted has been calculated from the information deposited with the Cambridge crystallographic data base.

(38) McNeill, E. A.; Scholer, F. R. *J. Am. Chem. Soc.* 1977, *99*, 6243.

(ethylene) distances (2.25 Å) are close to the corresponding X-ray results (2.22 (1) Å). The calculated C–Os–C angle for the equatorial carbonyls (107°) agrees very well with the corresponding X-ray result (106.0 (7)°). The calculations reproduce the slight tilt of the axial carbonyls toward ethylene, with a calculated axial C–Os–C angle of 172° that again agrees very well with the corresponding X-ray result (171.3 (5)°).

The geometry calculated for $Os(CO)_4$, the fragment remaining after ethylene loss from 1, is quite similar to that calculated for 1. The major geometric change is in the equatorial C–Os–C angle; these carbonyls bend toward the vacant coordination site by 28° upon removal of the ethylene. The axial carbonyls also bend toward the vacant coordination site after the ethylene of 1 is removed, but by only 1°.

Replacement of the ethylene in 1 by the two hydride ligands in $H_2Os(CO)_4$ causes substantially larger changes in the calculated geometry. The two equatorial carbonyls bend back by 7° in response to the increase in the X–Os–X angle from 37° (the C–Os–C angle spanned by the ethylene carbons in 1) to 85° (the H–Os–H angle in the dihydride). The axial carbonyls bend toward the hydride ligands by an additional 11°. The calculated carbonyl–Os–carbonyl angles are close to those estimated (94.3° equatorial, 161.3° axial for $H_2Os(CO)_4$ from unpublished electron diffraction data.[36].

Discussion

The scalar coupling constants of the ethylene ligand of 1 differ considerably from those of free ethylene (Table I). The geminal coupling constant $^2J_{HH}$, which becomes more negative as the H–C–H angle decreases, has a value in 1 (−9.9 Hz) not only below that in ethylene (+2.4 Hz) but below that in cyclopropane (−4.3 Hz) and almost down to that in methane (−12.4 Hz).[41]

The fact that scalar coupling constants involving carbon ($^1J_{CH}$ and $^1J_{CC}$) are usually proportional to fractional s character at carbon has been widely used (and abused). Although comparisons of these coupling constants between different compounds can be tricky, especially if different substituents are present,[42] their values can still be a useful guide to bonding in simple organic and organometallic systems.

The value of $^1J_{CH}$ for 1 in Table I (+158 Hz) lies in the narrow range between that for ethylene (+156 Hz) and that for cyclopropane (+160 Hz), showing that this parameter is quite insensitive to changes in metal–olefin bonding. This was first rationalized by Tolman,[43] who contrasted the small change in $^1J_{CH}$ between ethylene and cyclopropane with the considerable change in C–C bond *length*. The small angles of a three-membered ring lead to the shift of carbon s character into the C–H bonds and p character into the C–C bonds, so that the s character in the C–H bonds of cyclopropane is about equal to that of ethylene.[44] Thus, values of $^1J_{CH}$ in both weak π complexes (structure I in the Introduction) and metallacyclopropanes (structure II in the Introduction) are quite similar, showing a range of only 10–20 Hz.[8,45]

Table VI. $^1J_{CC}$ **and C–C Bond Lengths for Several Ethylene Complexes**

complex	$^1J_{CC}$ (Hz)	R_{CC} (Å)	ref
ethylene	67.6	1.335 (4)	*a, b*
$Cp^*Co(P(OMe)_3)(\eta^2\text{-}C_2H_4)\text{-}CH_2CH_3$	44		*c*
$[(Me_2PhP)_3Ir(\eta^2\text{-}C_2H_4)_2]^+$	41	1.40 (3)	*d*
	41	1.43 (2)	
$Os(CO)_4(C_2H_4)$ (1)	39	1.488 (24)	this work
$W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$	35	1.43 (2)	*e*
$W_2(OCH_2\text{-}t\text{-}Bu)_6(\eta^2\text{-}C_2H_4)_2$	28		*e*
$(Cy_3P)_2Pt(\eta^2\text{-}C_2H_4)$	31	1.440 (7)	*e, f*
cyclopropane	12.4	1.504 (4)	*g, h*
ethane	34.6	1.532 (2)	*a, i*

[a] Reference 18. [b] Kuchitsu, K. *J. Chem. Phys.* **1966**, *44*, 906. [c] Brookhart, M.; Volpe, A. F., Jr.; Lincoln, D. M.; Horvâth, I. T.; Millar, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 5634. [d] Lundquist, E. G.; Huffman, J. C.; Folting, K.; Caulton, K. G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1165. [e] Reference 45a. [f] Clark, H. C.; Hampden-Smith, M. J.; Furgerson, G.; Kaitner, B.; Ruegger, H. *Polyhedron* **1988**, *7*, 1349. [g] Reference 46. [h] Yamamoto, S.; Nakata, M.; Fukuyama, T.; Kuchitsu, K. *J. Phys. Chem.* **1985**, *89*, 3298. [i] Kuchitsu, K. *J. Chem. Phys.* **1968**, *49*, 4456.

In contrast, this shift of carbon s character out of strained rings helps make $^1J_{CC}$ a sensitive indicator of the nature of bonding in hydrocarbons: it is +67.6 Hz in ethylene,[18] +34.6 Hz in ethane,[18] and only +12.4 Hz in cyclopropane.[46] One might expect $^1J_{CC}$ to be a guide to the importance of a metallacyclopropane resonance structure in the bonding in an olefin complex. Values of $^1J_{CC}$ in coordinated olefins have been reported by von Philipsborn and co-workers for a series of η^4-diene, η^3-allyl, and η^2-ene complexes of Fe, Ru, and Os.[47–49] For acrolein, $^1J_{CC}$ decreases from +68 Hz in the free olefin to +45.2 Hz in (η^2-acrolein)$Fe(CO)_4$ and to +44.0 Hz in (η^2-acrolein)-$Ru(CO)_4$, suggesting a greater interaction with Ru than with Fe; the $^1J_{CC}$ values of $Fe(CO)_3$, $Ru(CO)_3$, and $Os(CO)_3$ η^4-diene complexes suggest that the interaction with osmium is strongest. Benn and co-workers have reported values of $^1J_{CC}$ (44–48 Hz) for several η^2-olefin–Ni(II) complexes.[50] Fitch, Ripplinger, Shoulders, and Sorey have measured $^1J_{CC}$ for a series of olefin complexes of Rh(I)[51] and have noted that these $^1J_{CC}$ values are influenced by substituent effects as well as by the hybridization of the orbitals used to form the C–C bond; they have suggested

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(39) Typical errors in C–C distances with a valence double ζ basis and Hartree–Fock wave function are ~0.02 Å,[40] and it is worth asking whether there is any reason for our calculated C–C distance to be short. As the true electronic structure of 1 is a linear combination of the two limiting electronic structures (an olefin π complex I and a metallacyclopropane II), inclusion of electron correlation would be necessary in order for the calculated geometric structure to be that observed experimentally. Knowledge of the energies of these two limiting electronic structures would be necessary in order to mix them correctly. The metal–carbon distances of metallocyclopropane II should have more correlation error, leading to an overestimate of the C–C distance calculated for that limiting structure; thus our calculations, by not including electron correlation, would be expected to overestimate the importance of π-complex form I and to underestimate the C–C distance.

(40) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986; Section 6.2.3, pp 146–164.

(41) Lambert, J. B.; Shurvell, H. F.; Verbit, L.; Cooks, R. G.; Stout, G. H. *Organic Structural Analysis*; McMillan: New York 1976; Chapter 4, pp 60–65.

(42) Gil, V. M. S. *Theor. Chim. Acta* **1989**, *76*, 291.

(43) Tolman, C. A.; English, A. D.; Manzer, L. E. *Inorg. Chem.* **1975**, 2353.

(44) A recent calculation (Honegger, E.; Heilbronner, E.; Schmelzer, A.; Jian-Qi, W. *Isr. J. Chem.* **1982**, *22*, 3–10) gives $sp^{1.94}$ for the carbon hybrid orbital used to form the C–H bonds in cyclopropane and $sp^{3.21}$ for the carbon hybrid orbital used to form the C–C bonds.

(45) (a) Chisholm, M. H.; Huffman, J. C.; Hampden-Smith, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 5284. (b) Fellmann, J. D.; Schrock, R. R.; Traficante, D. D. *Organometallics* **1982**, *1*, 481. (c) Fellmann, J. D.; Schrock, R. R.; Rupprecht, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 5752.

(46) Kalinowski, H.-O.; Berger, S.; Braun, S. *^{13}C-NMR-Spektroskopie*; Georg Thieme: New York, 1984; pp 444–461 and 496–504.

(47) Zobl-Ruh, S.; von Philipsborn, W. *Helv. Chim. Acta* **1981**, *64*, 2378.

(48) Zobl-Ruh, S.; von Philipsborn, W. *Helv. Chim. Acta* **1980**, *63*, 773.

(49) Adams, C. M.; Cerioni, G.; Hafner, A.; Kalchhauser, H.; von Philipsborn, W.; Prewo, R.; Schwenk, A. *Helv. Chim. Acta* **1988**, *71*, 1116.

(50) Benn, R.; Rufińska, A. *J. Organomet. Chem.* **1982**, C27.

(51) Fitch, J. W.; Ripplinger, E. B.; Shoulders, B. A.; Sorey, S. D. *J. Organomet. Chem.* **1988**, *352*, C25.

that $\Delta(^1J_{CC})$, the change in coupling constant between the free and the coordinated olefin, is a more accurate guide to the nature of the metal–olefin interaction than is the $^1J_{CC}$ value for the complex alone.

Although there are no substituents on the ethylene ligand in 1, it is still best to compare its value of $^1J_{CC}$ with that in other ethylene complexes and in free ethylene. We have attempted to collect in Table VI all known $^1J_{CC}$ values for coordinated ethylene along with the corresponding C–C bond lengths; we have also included the corresponding data for free ethylene and related organic compounds. (For most of the ethylene complexes in Table VI, $^1J_{CC}$ has been determined only because of the suspicion that they possess substantial metallacyclopropane character, so the range of $^1J_{CC}$ values they display is probably not representative of the range that would be spanned if such data were available for all ethylene complexes).

In general the C–C bond lengths in Table VI increase as $^1J_{CC}$ decreases. The $\Delta(^1J_{CC})$ between 1 and free ethylene (−28.6 Hz) is large enough to imply that the ethylene carbons have considerably rehybridized upon coordination to $Os(CO)_4$ and that 1 has considerable metallacyclopropane character. However, if we use $\Delta(^1J_{CC})$ as a criterion, several compounds in Table VI have *more* metallacyclopropane character than 1. The range of $^1J_{CC}$ values in Table VI extends below that of ethane itself (+34.6 Hz), suggesting that the decreased carbon s-orbital character that strain introduces into the C–C bonds of cyclopropanes is also present in *metalla*cyclopropanes.

Although the C–C bond length in 1 appears to be relatively long, the low precision with which it has been determined makes it difficult to use it in assessing the metallacyclopropane character of 1. The length of this bond in 1 cannot even be compared with that in other $M(CO)_4(C_2H_4)$ complexes, as the structure of $Ru(CO)_4(C_2H_4)$ (7) is unknown and that of $Fe(CO)_4(C_2H_4)$ (8) is only available as an electron diffraction structure of *very* low precision.[30a]

However, ab initio calculations have not only confirmed the metallacyclopropane nature of 1 but have explained why its axial carbonyl ligands bend toward the ethylene.

Theoretical Analysis of the Bonding in 1. The orbital amplitude contour diagrams for the uniquely defined orbitals of the GVB(6/12) wave function for 1 are given in Figure 3. The one-electron orbitals for the C–C σ bond pair (Figure 3a, in the equatorial plane) look like the sp^x hybrid orbitals of a carbon–carbon σ bond. The one-electron orbitals in the same plane for one of the Os–C σ bond pairs (Figure 3b) are quite similar to those obtained previously by Steigerwald and Goddard[7] for the Ti–C bond pairs of $Cl_2Ti(C_2H_4)$. The Os one-electron orbital in Figure 3b is predominantly d_σ but does not point directly at the carbon due to the strain inherent in the three-membered ring. The angle between the two Os-centered d_σ orbitals (which form the two Os–C bonds) is 75°—the same angle obtained by Steigerwald and Goddard for the two Ti-centered d_σ orbitals of $Cl_2Ti(C_2H_4)$.[7] Finally, the carbon-centered one-electron orbital in Figure 3b is particularly instructive. In the limit of the π-complex resonance structure I, this carbon-centered orbital would be a pure p orbital; in the limit of the metallacyclopropane resonance structure II it would be an sp^x hybrid. The orbital in Figure 3b has substantially less p character than the corresponding orbital of Steigerwald and Goddard for $Cl_2Ti(C_2H_4)$,[7] implying that the carbon centers in 1 are significantly more sp^x hybridized than those in $Cl_2Ti(C_2H_4)$ and that 1 is even more of a metallacyclopropane than the titanium ethylene complex.

Table V also shows the calculated C–H bond length and H–C–H angle for 1. Although they cannot be compared with experimental values from Table IV because the hydrogen atoms were not located in the X-ray structure determination, they can be compared to the experimental values determined by nematic phase NMR;[10] a detailed analysis of the geometry determined for the coordinated ethylene in 1 by this method has confirmed the metallacyclopropane character of 1.[10]

The reasons why the axial carbonyls in 1 bend toward the ethylene become clear when we use the contour diagrams to see what happens to all the osmium d orbitals as the ethylene is bound. Of the three d orbitals on Os with nonzero amplitudes in the equatorial plane, two are the Os-centered d_σ orbitals discussed above; the third is the conventional doubly occupied nonbonding orbital shown in Figure 3c.

The remaining two d orbitals are equivalent and purely π with respect to the equatorial plane. Figure 3d shows the orbital amplitude of one of them plotted in the plane that passes through the Os and the C of one of the two equatorial carbonyls, is perpendicular to the equatorial plane, and nearly passes through the axial carbonyl ligands. It is apparent that this orbital is a conventional four-lobed d orbital with a small component of delocalization into the π^* orbital of the equatorial carbonyl. Its left and right pairs of lobes are asymmetric due to the mixing in of virtual p_π character.

The same d_π orbital is replotted in Figure 3e for a distorted geometry of 1 wherein the axial carbonyls are forced to be trans (C–Os–C angle = 180°). This distortion raises the energy of the complex by 1.4 kcal/mol and removes the left–right asymmetry of the orbital lobes, thus decreasing the delocalization into the π^* orbital of the equatorial carbonyl. The tilt of the axial carbonyls toward the ethylene of 1, which causes this d_π orbital to look like Figure 3d rather than Figure 3e, thus permits increased back-bonding to the equatorial carbonyls.

This analysis implies that there is greater back-bonding from osmium to the equatorial carbonyls than to the axial ones. It thus predicts that the equatorial Os–C distance should be shorter than the axial Os–CO distance (the calculated equatorial Os–C distance is 1.97 Å, whereas the calculated axial one is 1.99 Å). Unfortunately the precision of the X-ray results does not permit us to be sure whether or not this prediction is correct.

Our analysis predicts that the axial carbonyls in $Os(CO)_4L$ should tilt toward all L that are less effective π acceptors than CO, and it is thus not surprising that Table V shows little change in the calculated tilt angle as ethylene is removed from 1, leaving $Os(CO)_4$ with a vacant coordination site. However, our analysis also predicts that the tilt angle will increase if more Os → (equatorial)CO back-bonding than that in 1 is needed. The trans influence of the σ-donor hydride ligands in $H_2Os(CO)_4$ should produce such an increase in the back-bonding required of the equatorial carbonyls, so it is not surprising that replacement of the ethylene of 1 by the two hydride ligands of $H_2Os(CO)_4$ leads to a substantial increase in the tilt angle (Table V).

Comparison with Published Results. Lindner and co-workers originally suggested[52a] that $Ru(CO)_4(C_2H_4)$ (7), the ruthenium analogue of 1, was *not* a ruthenacyclopropane because of its ^{13}C chemical shifts. However, the same group later noted[52b] that the product of the reaction

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(52) (a) Lindner, E.; Jansen, R.-M.; Mayer, H. A. *Angew. Chem., Int. Ed. Engl.* 1986, *25*, 1008. (b) Lindner, E.; Jansen, R.-M.; Mayer, H. A.; Hiller, W.; Fawzi, R. *Organometallics* 1989, *8*, 2355.

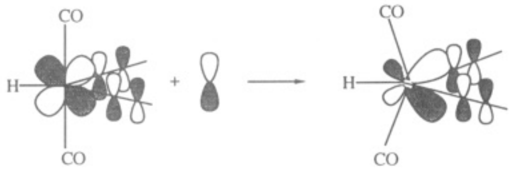

Figure 6. Orbital mixing in $HCo(CO)_4$ (from ref 56).

of 7 with hexafluoro-2-butyne suggested that the reaction had begun with an insertion reaction of the sort characteristic of a metallacyclopropane. PRDDO (partial retention of diatomic differential overlap) calculations (using the Boys localization procedure) on the iron analogue of 1, $Fe(CO)_4(C_2H_4)$ (8), have suggested that the dominant resonance structure of 8 is a metallacyclopropane.[53]

The suggestion[34] that π donation by the bis(trimethylsilyl)acetylene ligand is an important reason for the tilt of the axial carbonyls in $(\eta^2\text{-}Me_3SiC_2SiMe_3)Os(CO)_4$ (**5**) toward the acetylene appears incorrect. While Ball, Burke, and Takats noted a tilt of the axial CO ligands *away* from the coordinated olefin in two $(\eta^2\text{-olefin})Fe(CO)_4$ complexes with bulky olefins,[54] a tilt in this direction is the result of steric effects. The tilt of the axial carbonyls *toward* the unsubstituted ethylene in 1 illustrates that *electronic* effects will bend the axial carbonyls in $LM(CO)_4$ complexes toward *any* L that is a less effective π acceptor than CO. As the calculated energy of distortion to an axial C–Os–C angle of 180° is only 1.4 kcal/mol, it is not surprising that sterically encumbered ligands L can overcome this electronic effect and cause axial carbonyls to bend away from L.

Other workers have also investigated the reasons why axial carbonyls bend toward ligands that are not π acceptors. The seminal work of Elian and Hoffmann on metal carbonyl fragments[55] addressed distortion of $M(CO)_4$ fragments but did not specifically discuss *axial* bending. Ziegler and co-workers have published LCAO-HFS calculations[56] for $HCo(CO)_4$ that describe a mixing of the metal d_{yz} orbital with an empty metal $4p_z$ orbital to give a metal dp hybrid which enhances back-bonding to the equatorial carbonyls (Figure 6). Eisenstein, Crabtree, and co-workers have more recently noted this d–p mixing using EHT.[57]

Conclusions

We have confirmed the dominance of metallacyclopropane character in 1 and provided an explanation for the observed distortion of its axial carbonyl ligands. In addition we have documented, by comparison with its X-ray structure, the geometric accuracy of ab initio calculational methods for third row transition metal complexes and have demonstrated the utility of the Krauss–Stevens[22] carbon and oxygen effective core potentials.

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Supplementary Material Available: Tables of anisotropic thermal parameters and H coordinates for 1 (2 pages). Ordering information is given on any current masthead page.

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[54] Ref 31 in ref 34: (a) η^2-acenaphthalene: Cotton, F. A.; Lahuerta, P. *Inorg. Chem.* **1975,** *14,* 116. (b) η^2-furanone: Chisnall, B. M.; Green, M.; Hughes, R. P.; Wells, A. J. *J. Chem. Soc.,* Dalton *Trans.* **1976,** 1899.

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Double Metalation and Iron–Osmium Bonding Involving Ferrocenyl Moieties on Clusters. Crystal and Molecular Structures of $H_2Os_3(CO)_8[(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_3PPr^i_2)]$ and $H_2Os_3(CO)_8[(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_3PFcEt)]$

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Thermolysis of $Os_3(CO)_{11}(PFcPr^i_2)$ and $Os_3(CO)_{11}(PEtFc_2)$ ($FcH = Fe(\eta\text{-}C_5H_5)_2$) affords the title compounds, $\{\mu_3\text{-}[(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_3PPr^i_2)]\}(\mu\text{-}H)_2Os_3(CO)_8$ (7) and $\{\mu_3\text{-}[(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_3PEtFc)]\}(\mu\text{-}H)_2Os_3(CO)_8$ (8), in 15 and 25% yield, respectively. The structures of 7 and 8 are very similar and they both contain a doubly metalated ferrocenyl moiety, the iron atom of which is bonded to one osmium atom in the cluster. 7: triclinic, $a = 10.262$ (3), $b = 15.538$ (2), $c = 9.837$ (3) Å, $\alpha = 98.21$ (2), $\beta = 117.85$ (2), $\gamma = 98.59$ (2)°, $Z = 2$, space group $P\bar{1}$. 8: monoclinic, $a = 10.356$ (3), $b = 19.514$ (3), $c = 15.630$ (3) Å, $\beta = 102.23$ (2)°, $Z = 4$, space group $P2_1/n$. The structures were solved by heavy-atom methods and were refined by full-matrix least-squares procedures to $R = 0.025$ and 0.032 for 6294 and 5234 reflections with $I \geq 3\sigma(I)$, respectively.

The thermolysis of tertiary ferrocenylphosphine derivatives of $Os_3(CO)_{12}$ has been used successfully to prepare 1, a cluster derivative of the previously unknown ferrocyne.[1] Other new classes of complexes were also recently

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