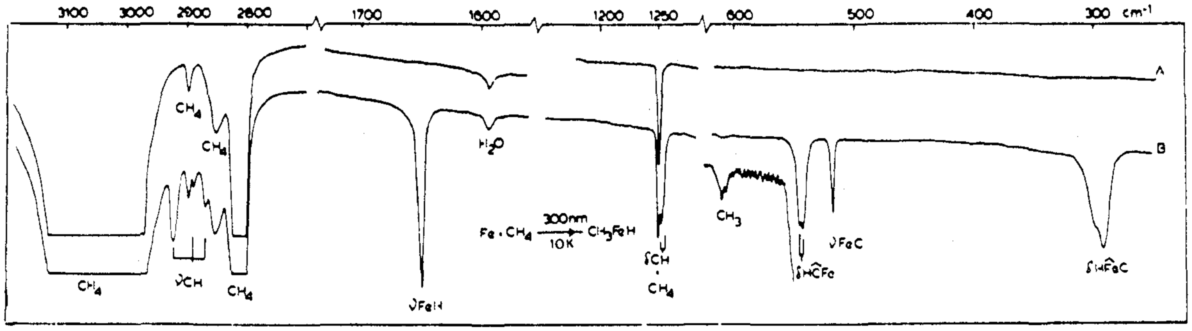
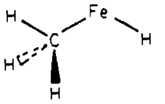
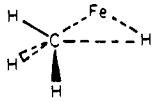


Figure 2. Infrared spectrum of Fe/CH_4 $(\simeq 1/10^4)$: (A) following deposition at 10–12 K showing only CH_4 bands; (B) following 300 min of 300-nm photolysis (same experimental arrangement as used in Figure 2 showing CH_3FeH product bands (negligible amounts of CH_3 radicals are formed in the above processes as seen from high sensitivity scans in the 600–620-cm^{-1} region (10× ordinate expansions). Note that the total amount of Fe deposited in the UV-visible experiments required to obtain data of the type typified by those shown in Figure 1 is about 5 times less than that needed to obtain the corresponding infrared spectroscopic data).

deriving from modes that would be doubly degenerate (E) for a linear C_{3v} molecule while nondegenerate (A′ + A″) for a nonlinear C_s molecule. On the basis of the observation that the former modes appear in the IR spectra as sharp singlets whereas the latter modes are all split into doublets (Figure 2B), it can be tentatively concluded that a nonlinear geometry prevails for CH_3FeH in solid CH_4. It is also pertinent to note that no evidence was obtained for species such as CH_3Fe, FeH, CH_3, or H during the 420-nm photolysis of CH_3FeH. The observation of a single "normal" ν_{FeH} stretching mode without any sign of a "softened" ν_{CH} mode (expected to occur in the 2690–2420-cm^{-1} region[6]) argues in favor of the formal insertion product I rather than the plausible alternative activated species II. One can therefore surmise that 420-nm photoexcitation of nonlinear CH_3FeH populates a low lying electronic state having antibonding character with respect to the C–Fe–H framework, which in a nonlinear configuration leads to a facile and concerted reductive elimination of CH_4 in much the same way as that postulated to occur in the concerted, photoinduced reductive elimination of H_2 from $(\eta^5\text{-}C_5H_5)_2MoH_2$, $IrClH_2(PPh_3)_3$, and $IrH_3(PPh_3)_3$ complexes.[3]


I


II

Finally, it is pertinent to note that the photoinduced reductive elimination of Fe atoms and CH_4 from CH_3FeH can be viewed as the microscopic reverse of the photoinsertion of Fe atoms into a CH bond of CH_4 to produce CH_3FeH. The system therefore provides the first "ligand free" model with which to experimentally probe the individual steps in a number of transition-metal-catalyzed processes,[4] as well as to theoretically evaluate which physically interpretable features of the local electronic structure of the metal determine chemical reactivity in the Fe/CH_4 and related M/alkane systems.[5]

Acknowledgment. The generous financial assistance of the Natural Sciences and Engineering Research Council of Canada's Strategic Energy Programme is greatly appreciated. In addition J.G.M. expresses his gratitude for a University of Toronto Open Scholarship.

Registry No. CH_3FeH, 83615-51-4; Fe, 7439-89-6; CH_4, 74-82-8.

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Substrate Organometallic Chemistry of Osmium Tetraoxide: Formation of a Novel Type of Carbon Dioxide Coordination

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As part of our general interest in the chemistry available to oxidizing compounds we have begun to investigate the principal interactions available to osmium tetraoxide and related molecules with classical organometallic entities such as Vaska's complex, *trans*-$IrCl(CO)(PPh_3)_2$. In this communication we report on the result of the oxidative-addition reaction of osmium tetraoxide to Vaska's complex in the presence of pyridine bases, a reaction that yields a dinuclear carbon dioxide adduct. This result provides a first glimpse at the substrate organometallic chemistry of osmium tetraoxide. A new type of carbon dioxide coordination has been discovered here.[2]

When 1 equiv of Vaska's complex is added to osmium tetraoxide in toluene at −78 °C and the mixture is allowed to warm to room temperature, a gradual color change from yellow to orange-brown occurs. A brown powder can be isolated by precipitation with hexanes, and orange-brown crystals of the air stable compound I (see Scheme I) form upon recrystallization from dichloromethane–*tert*-butylpyridine–di-*n*-butyl ether. Compound I reacts readily at room temperature with *tert*-butyl isocyanide in dichloromethane to give the air-stable olive-green dinuclear salt, II, in high yield. We assume the coordination environment at iridium in II is as depicted in the scheme since treatment of II

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[2] Structurally characterized carbon dioxide complexes include $Ni(\eta^2\text{-}CO_2)(PCy_3)_2$ (Aresta, M.; Nobile, C. F.; Albano, V. G.; Forni, E.; Manassero, M. *J. Chem. Soc., Chem. Commun.* **1975**, 636. Aresta, M.; Nobile, C. F. *J. Chem. Soc., Dalton Trans.* **1977**, 708), $[Co(pr\text{-}salen)K(\mu\text{-}CO_2)(THF)]_n$ (Fachinetti, G.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1978**, *101*, 74), $[(Ph_3P)_2N][HOs_3(CO)_{10}{\cdot}O_2COs_6(CO)_{17}]$ (Guy, J. J.; Sheldrick, G. M. *Acta Crystallogr., Sect. B* **1978**, B34, 1718), and $Nb(\eta^5\text{-}C_5H_4Me)_2(CH_2SiMe_3)(\eta^2\text{-}CO_2)$ (Bristow, G. S.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1981**, 1145.

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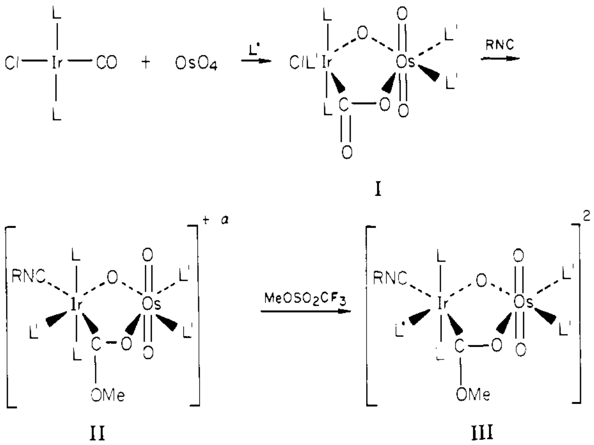
Scheme I



L = triphenylphosphine
L' = 4-*tert*-butylpyridine
R = *tert*-butyl

[a] Isolated and characterized as the perchlorate salt.

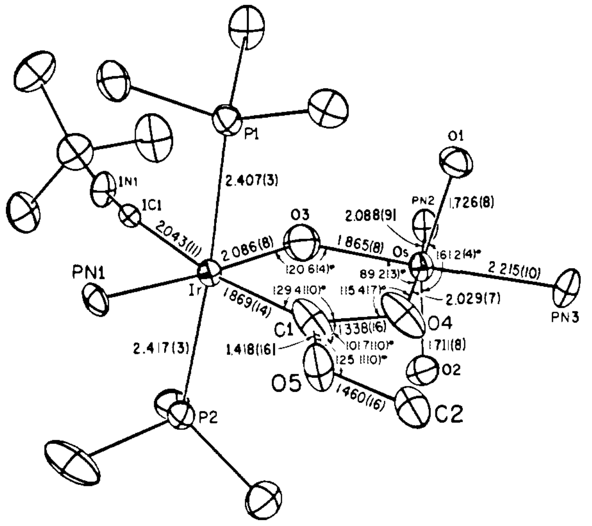


Figure 1. Molecular structure of the dication $[(PPh_3)_2(t\text{-BuNC})(4\text{-}t\text{-Bupy})Ir(\mu\text{-O})(\mu\text{-C[OMe]O})Os(O)_2(4\text{-}t\text{-Bupy})_2]^{2+}$.

with methyl trifluoromethanesulfonate in dry benzene yields a brown precipitate which, after perchlorate exchange, affords brown crystals of the air-stable carbene-containing compound III.[3] An X-ray crystal structure analysis of III is consistent with methylation proceeding at the exocyclic oxygen atom of the bridging carbon dioxide moiety (see Figure 1).[4] The *O*-methyl and nonmethylated oxygen atoms of the carbene ligand are cis, and NMR evidence (−70 to 40 °C) suggests either the presence of only one of the two possible carbene isomers in solution or free rotation about the C1–O5 bond occurring in solution.

Table I. ^{31}P and ^{13}C NMR Data[a] (δ)

compd	^{31}P,[b] δ	^{13}C,[c] δ	$^2J_{^{13}C-^{31}P}$, Hz[d]
I	−14.0	187.2	7.0
II	−18.2	207.5	8.8
III	−19.2	221.1	8.8

[a] JEOL FX 90Q, solvent $CDCl_3$. [b] Relative to external standard H_3PO_4. [c] Relative to internal standard Me_4Si. [d] Obtained from ^{13}C and ^{31}P spectra.

Table II. Relevant Infrared Data (cm^{-1})

compd	$\nu_{C=O}$	ν_{C-O}	ν_{OsO_2}	$\nu_{N\equiv C}$
I	1593	1022	820	
I-^{13}C	1560	1010	820	
I-^{18}O	1592	1010	780	
II	1583	*a*	823	2180
II-^{13}C	1555	*a*	823	2180
II-^{18}O	1583	*a*	785	2180

compd	CO_2Me	ν_{OsO_2}	$\nu_{N\equiv C}$
III	1255	840	2200
III-^{13}O	1230	840	2200
III-^{18}O	1255	800	2200

[a] Obscured by ClO_4^- bands.

The formulation of compounds I and II as dinuclear bridging carbon dioxide complexes follows from the X-ray analysis of III and is additionally supported by the appropriate ^1H, ^{31}P, and ^{13}C NMR spectra and by IR experiments with ^{13}C- and ^{18}O-labeled materials (see Tables I and II). Label enrichment was based on the use of *trans*-$IrCl(^{13}CO)(PPh_3)_2$ (99% enriched) and $Os^{18}O_4$ (88% enriched), and the IR bands corresponding to the bridging CO_2 ligand have been identified by the isotopically induced band shifts. The ν(C=O) band for I at 1593 cm^{-1} shifts to 1560 cm^{-1} upon ^{13}C substitution. A similar shift is observed for II. A band at 1022 cm^{-1} in I shifts to 1010 upon ^{13}C or ^{18}O substitution, confirming that the bridging carbon dioxide ligand is constructed from the iridium carbonyl ligand and the oxo ligand from osmium tetraoxide. The coordination at the osmium center is also well characterized from the IR spectral data. The very strong trans-$Os^{16}O_2$ asymmetric stretching band can be identified at 820, 823, and 840 cm^{-1} for compounds I–III, respectively. These bands fall in the expected region[5] and have been confirmed by isotopic substitution.

The ^{13}C and ^{31}P NMR spectra provide evidence for the presence of equivalent phosphine ligands in each compound. The ^{13}C-enriched carbon dioxide signal in I is a triplet at δ 187.2 ($^2J_{^{13}C-^{31}P}$ = 7.0 Hz), which shifts to δ 207.2 in II and δ 221 in III.[6] The ^1H NMR spectra of compounds I and II exhibit considerable temperature dependence. Our evidence suggests this feature is due to lability of the *tert*-butylpyridine ligands on osmium(VI) but not to lability at the iridium center. We will describe this chemical property more fully at a later date.

The X-ray crystal structure of III shows the expected existence of multiple bonding between the carbene carbon atom and the oxygen hetero atoms. It is interesting to note that the C1–O4 bond length [1.338 (16) Å] is significantly shorter than the C1–O5 bond length [1.418 (16) Å] suggesting that the CO_2Me unit might also be described as a bridging ester ligand.

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Supplementary Material Available: Listings of fractional atomic coordinates, Gaussian amplitudes, bond distances and angles, and structure factor amplitudes (62 pages). Ordering information is given on any current masthead page.

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(3) Elemental analysis data: all solvates quantified by NMR. Calcd for $I\cdot{}^1/_3Bu_2O$: C, 53.97; H, 5.10; N, 2.83. Found: C, 54.15; H, 5.29; N, 2.80. Calcd for $II\cdot H_2O$: C. 51.63; H 5.02; N, 3.49. Found: C, 51.49; H, 4.95; N, 3.53. Calcd for $III\cdot 1.25H_2O$ (0.25, CH_2Cl_2): C, 48.34; H, 4.85; N, 3.21. Found: C, 48.33; H, 4.81; N, 3.21.

(4) Crystal data: space group $P\bar{1}$, a = 21.20 (2) Å, b = 12.800 (5) Å, c = 14.470 (16) Å, α = 85.78 (9)°, β = 94.04 (9)°, γ = 94.41 (9)°, V = 3896 $Å^3$, Z = 2. Data were collected on a locally modified Syntex $P2_1$ diffractometer with graphite monochromator and Mo Kα radiation (λ 0.71069 Å) to 2θ = 48° ($+h\pm k\pm l$). The averaged data (10 222) were corrected for Lorentz and polarization effects. The Os and Ir atom positions were derived from the Patterson map, and subsequent Fourier maps revealed the remaining non-hydrogen atoms. Least-squares refinement of atomic coordinates and B's, minimizing $\sum w[F_o^2 - (F_c/k)^2]^2$ with weights $w = [\sigma^2(F^2) + (0.02 \times \text{scan counts})^2]^{-1}$ gave $R_F = \sum||F_o| - |F_c||/\sum|F_o|$ = 0.13 (9268 reflections with $F_o^2 > 0$). Introduction of hydrogen atoms from difference maps with B = 5 $Å^2$ and refinement of all nonhydrogen atoms with anisotropic Gaussian amplitudes resulted in R_F = 0.086 and GOF = 1.66 (R_f = 0.055 for the 6347 reflections with $F_o^2 > 3\sigma(F^2)$).

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(6) The ^{13}C NMR signal for the CO_2 ligand in $Nb(\eta^5\text{-}C_5H_4Me)(CH_2SiMe_3)(\eta^2\text{-}CO_2)$ occurs at δ 200.5.[2]