

Synthesis and Structure Determination of
 $\text{Os}_3[1,2-\mu\text{-H}; 1,2-\mu\text{-O}=\text{C}(\text{Me})]\{1\text{-C}(\text{OMe})\text{Me}\}(\text{CO})_9$:
The First Cluster Complex Containing a Fischer-Type
Carbene Group

C. M. Jensen, T. J. Lynch, C. B. Knobler, and H. D. Kaesz*

Department of Chemistry and Biochemistry
 University of California, Los Angeles, California 90024

Received May 10, 1982

Spectroscopic study of the reactions of $\text{Os}_3(\text{CO})_{12}$, **1**, with anionic nucleophiles indicates that these attack at the carbon atom of a coordinated CO to give $\eta^1\text{-C}(\text{O})\text{Nu}$ -substituted trinuclear anions.¹ It was of interest to alkylate the anion where $\text{Nu} = \text{R}^-$, which was expected to lead to a cluster complex containing a Fischer-type carbene.² In the 18 years since the isolation of the first heterocarbene complex by Fischer and Maasböl,^{2c} no cluster complex containing such a functional group has been reported.^{3,4} Indeed, our attempts to alkylate $[\text{Li}][\text{Os}_3\{\eta^1\text{-C}(\text{O})\text{CH}_3\}(\text{CO})_{11}]$, **2**, in tetrahydrofuran (THF) proved unsuccessful.⁵ By contrast, alkylation of $[\text{PPN}][\text{Os}_3\{1,2-\mu\text{-O}=\text{C}(\text{CH}_3)\}(\text{CO})_{10}]$, **3**,⁶ gives a product that is converted to the title compound when subjected to chromatography on silica gel.⁷ We were thus prompted to

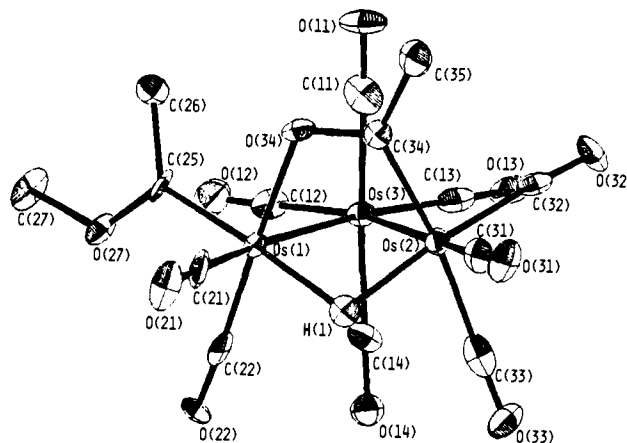
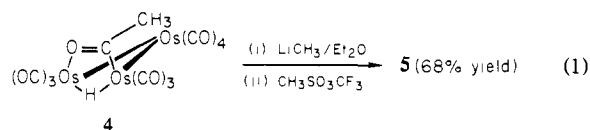


Figure 1. ORTEP projection of $\text{Os}_3[1,2-\mu\text{-H}; 1,2-\mu\text{-O}=\text{C}(\text{Me})]\{1\text{-C}(\text{OMe})\text{Me}\}(\text{CO})_9$, thermal ellipsoids at 50% probability. Selected bond lengths (Å): Os(1)–Os(2), 2.934 (2); Os(1)–Os(3), 2.852 (1); Os(2)–Os(3), 2.892 (1); Os(1)–C(25), 1.99 (2); C(25)–C(26), 1.51 (3); C(25)–O(27), 1.34 (2); O(27)–C(27), 1.45 (2); Os(2)–C(34), 2.04 (2); C(34)–C(35), 1.53 (3); C(34)–O(34), 1.29 (2); Os(1)–O(34), 2.13 (1). Selected bond angles (°): O(27)–C(25)–C(26), 117 (1); O(27)–C(25)–Os(1), 120 (1); C(26)–C(25)–Os(1), 124 (1); C(25)–O(27)–C(27), 122 (1); O(34)–C(34)–C(35), 113 (2); O(34)–C(34)–Os(2), 113 (1); C(35)–C(34)–Os(2), 128 (1); C(34)–O(34)–Os(1), 108 (1).

synthesize the title compound directly from the hydrido/acyl-bridged complex **4** as summarized in eq 1 and described below.



$\text{Os}_3[1,2-\mu\text{-H}; 1,2-\mu\text{-O}=\text{C}(\text{Me})](\text{CO})_{10}$, **4**, (100 mg, 11.2 μmol) in 50 mL of dry freshly distilled diethyl ether is titrated with CH_3Li (1.6 N in diethyl ether) at 0 °C until the IR absorptions of **4** disappear. $\text{CH}_3\text{SO}_3\text{CF}_3$ (13.6 μL , 12.0 μmol) is added and the solution brought to room temperature. After being stirred for 36 h, the solvent is removed under vacuum. The ^1H NMR spectrum of the residue dissolved in CDCl_3 indicates presence of the title compound, **5** in major yield. The mixture is separated by column chromatography on silica gel. Eluting with petroleum ether results in isolation of two minor products along with 11 mg of starting material.⁸ Further elution with CH_2Cl_2 results in the isolation of the pure, air- and moisture-stable title compound **5**, an orange material, in 68% yield.⁹

A crystal of **5** suitable for X-ray diffraction was obtained by slow evaporation from pentane solution and its structure determined from data collected at –158 °C;¹⁰ an ORTEP projection is

(7) The first formed product in the alkylation of $[\text{Os}_3\{\mu\text{-C}(\text{O})\text{CH}_3\}(\text{CO})_{10}]^-$ is a highly unstable species that has thus far been characterized only by ^1H NMR in reaction mixture at 0 °C. This spectrum contains only a singlet at δ 2.58; with the PPN resonances as reference, this peak shows twice the intensity of the methyl acetyl resonance of the starting material. Attempted purification by chromatography gives rise to **4** and **5** as well as a third product in roughly equal amounts. The latter is identified as $\text{Os}_3[1,2-\mu\text{-OH}; 1,2-\mu\text{-O}=\text{C}(\text{Me})](\text{CO})_{10}$, by the following spectroscopic data: IR (ν_{OH} , KBr) 3625 w, 3436 w (br); IR (ν_{CO} , hexane) 2104 m, 2071 s, 2051 s, 2020 s, 2007 s, 1988 s, 1974 m; ^1H NMR (CDCl_3) δ 2.74; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 295.5, 187.3, 183.9, 182.4, 180.1, 178.7, 178.1, 177.5, 175.9, 169.1, 168.5, 50.8). The mass spectrum of this material shows a parent peak minus one carbonyl at m/e 882 with fragment ions corresponding to loss of eight CO groups.

(8) The two minor products obtained in 6.8- and 8.2-mg quantities, respectively, have not yet been characterized.

(9) Spectroscopic data for **5**: mass spectrum shows parent ion m/e 924 and fragment ions corresponding to successive loss of nine CO's; IR (hexane, ν_{CO} , cm^{-1}) 2093 m, 2052 s, 2022 vs, 2001 m, 1991 m, 1973 m, 1961 w, 1950 m; IR (KBr, $\nu_{\text{C}(\text{carbene})\text{O}}$) 1291 m; ^1H NMR (CDCl_3) δ 4.33 (s, 3), 2.56 (s, 3), 2.33 (s, 3), –1.520 (s, 1); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 282.4, 266.7, 186.2, 182.2, 181.7, 178.6, 178.2, 176.5 (approximately double in intensity of the other resonances), 175.5, 174.8, 65.1, 50.2, 32.3.

(1) Mayr, A.; Lin, Y. C.; Boag, N. M.; Kaesz, H. D. *Inorg. Chem.* **1982**, *21*, 1704–1706.

(2) (a) Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1–32. (b) Fischer, E. O.; Schubert, U.; Fischer, H. *Pure Appl. Chem.* **1978**, *50*, 857–870. (c) Fischer, E. O.; Maasböl, A. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 580–581.

(3) Fischer-type carbene groups have been synthesized on dimeric metal complexes where they appear in a terminally bonded position as in a, b, or c or in bridged bonding positions as in d: (a) $\text{M}_2[\text{C}(\text{OMe})\text{R}](\text{CO})_9$, M = Tc or Re; R = Me or Ph; $\text{M}_2 = \text{ReMn}$; R = Ph: Fischer, E. O.; Offhaus, E.; Müller, J.; Nöthe, D. *Chem. Ber.* **1972**, *105*, 3027–3035. (b) *cis*- $\text{Re}[\text{C}(\text{OMe})\text{Me}](\text{CO})_4\text{Mn}(\text{CO})_5$: Casey, C. P.; Cyr, C. R.; Anderson, R. L.; Marten, D. F. *J. Am. Chem. Soc.* **1975**, *97*, 3053–3059. (c) $\text{Re}_2[\mu\text{-C}(\text{OMe})\text{Ph}]_2(\text{CO})_8$: Fischer, E. O.; Lindner, T. L.; Fischer, H.; Hüttner, G.; Friedrich, P.; Kreissl, F. R. *Z. Naturforsch. B* **1977**, *32B*, 648–652; (d) $\text{Re}_2[\text{C}(\text{OEt})\text{SiPh}_3]_2(\text{CO})_8$ and $\text{Re}[\text{C}(\text{OEt})(\text{tolyl})][\text{C}(\text{OEt})\text{SiPh}_3](\text{CO})_8$: Fischer, E. O.; Rustmeyer, P. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 627–630.

(4) Alkylidene carbene groups are known on triosmium centers where spectroscopic and/or structural data indicate these to occupy bridging positions: (a) Steinmetz, G. R.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 1279–1281. (b) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5225–5226 (corrected **1978**, *100*, 6544). (c) Shapley, J. R.; Sievert, A. C.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 6975–6977.

(5) (a) A solution of **2** is prepared by titration of **1** in THF at 0 °C with LiCH_3 in diethyl ether followed to the disappearance of the IR absorptions of **1**. This solution, which shows the absorptions of **2** (cf. ref 1), is warmed to room temperature, and $\text{CH}_3\text{SO}_3\text{CF}_3$ is added. The spectrum shows very little change (a diminishing intensity of bands near 1966 cm^{-1}) over a period of 4 h. While alkylation is thus slow in the THF/ether solvent system, attempts to exchange for a less basic solvent lead to formation of the μ -acyl anion (see footnote 6 below). After 4 h of attempted alkylation, solvent is removed under vacuum and the residue taken up in benzene-*d*₆. Evidence for an unstable THF adduct, presumably $\text{Os}_3(\text{CO})_{11}(\text{THF})$, is obtained in the ^1H NMR, which displays resonances at δ 3.43 (t, 1) and 1.77 (q, 1). For verification of this assignment excess THF is added to the solution; resonances of both the coordinated and free THF (δ 3.65 (t, 1), 1.50 (q, 1)) are observed. GC analysis of aliquots of the alkylation mixture shows acetaldehyde to be present reaching a stoichiometric amount after about 8 h. These products indicate that alkylation of **2** is very slow in THF/ether and that alkylation of the THF (to give trifluoromethylsulphonic acid)^{6b} is a competitive process under these conditions. Protonation by acid either at the oxygen or at the metal of $[\text{Os}_3\{\eta^1\text{-C}(\text{O})\text{CH}_3\}(\text{CO})_{11}]^-$ obviously leads to an unstable material which could give the two products observed. (b) Gramstad, T.; Haszeldine, R. N. *J. Chem. Soc.* **1957**, *90*, 4069–4079.

(6) (a) A solution of the $[\text{PPN}]^+$ salt is prepared by adding a slight excess of $[\text{PPN}][\text{Cl}]$ ^{6b} to a THF solution of **2** followed by stirring for 24 h, during which time CO is slowly evolved to give the bridged acyl group.¹ This process is brought to completion when the THF is removed under vacuum and replaced by chloroform; several cycles of solvent removal and replacement may be needed. (b) $[\text{PPN}][\text{Cl}] = \text{bis}(\text{triphenylphosphine})\text{iminium chloride}$; Alpha Division, Ventron, Danvers, MA 01923. Chemical Abstracts recommended name for $[\text{PPN}]^+$ is bis(triphenylphosphorane)nitrogen(1+).

shown in Figure 1. This consists of a triangle of osmium atoms bridged on the longest edge by an acetyl group and a hydrogen atom.¹¹ The carbene group is terminally bonded to Os(1), to which is also coordinated the oxygen of the bridging acetyl group. The bond distances from C(25), the carbenoid carbon atom, to Os(1) and to the methoxy oxygen and the methyl carbon atoms as well as the angles about C(25) are all typical of those found in Fischer-type carbene complexes² (see caption to Figure 1).

Our work clarifies for the first time the rarity of the Fischer carbene groups on metal clusters. This derives from the chemical properties of the η^1 -C(O)R group formed in the attack of nucleophile on the cluster. In the medium needed to form such a group, alkylation is very slow; in attempts to exchange solvent, the labilizing influence of the η^1 -C(O)R group leads to loss of CO and formation of the bridged μ -O=C(R) complex. It is ironic that synthesis of the Fischer carbene takes place on a hydrido-cluster complex, which gives some idea of the relative tendencies for competing processes such as attack by nucleophile on coordinated CO as opposed to removal of bridging hydrogen as proton.

Acknowledgment. This work has been supported by a grant from the National Science Foundation (No. CHE 79-08406).

Registry No. 4, 65908-54-5; 5, 82390-92-9; CH₃Li, 917-54-4; CH₃S-O₃CF₃, 333-27-7.

(10) Orange crystals are monoclinic, space group $P2_1/n$, $a = 9.578$ (4) Å, $b = 13.494$ (4) Å, $c = 15.187$ (6) Å, $\beta = 96.30$ (3)°; $V = 1951$ (1) Å³, $Z = 4$, $\rho_{\text{calc}} = 3.15$ g cm⁻³ (MoK $\alpha = 0.71069$ Å³). The structure was solved and refined by using 2728 observed ($I > 3\sigma(I)$) independent reflections measured on a Syntex P1 automated diffractometer in the range $0^\circ < 2\theta < 50^\circ$. An absorption correction was applied ($\mu = 195.66$ cm⁻¹). Refinement converged at $R = 0.050$ and $R_w = 0.061$.

(11) After all non-hydrogen atoms were refined anisotropically, the metal hydride was located and refined.

Dichlorine Monoxide: A Powerful and Selective Chlorinating Reagent[†]

F. D. Marsh,* W. B. Farnham,* D. J. Sam, and B. E. Smart



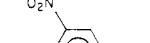
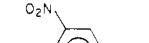

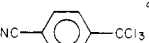
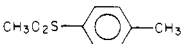
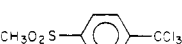
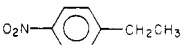
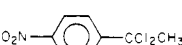
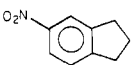
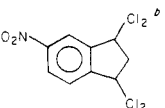
*E. I. du Pont de Nemours and Company
Experimental Station
Central Research and Development Department
Wilmington, Delaware 19898*

Received April 29, 1982

Dichlorine monoxide (Cl₂O) has long been known¹ and has been the subject of some modern mechanistic² and physical³ studies, but it has not been shown to be a useful reagent in synthetic chemistry. We have found that Cl₂O is a powerful and selective reagent for either side-chain or ring chlorination of deactivated aromatic substrates, and it gives excellent yields under mild conditions where conventional reagents fail or require harsh conditions.

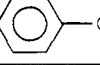
The free-radical, side-chain chlorinations of deactivated alkyl aromatic compounds such as *p*-nitrotoluene normally require high temperatures and give largely benzyl chlorides and hydrochloric acid.⁴ Only small amounts of benzal chlorides and little or no benzotrichlorides are produced.⁵ More forcing conditions lead

Table I. Chlorination of Deactivated Alkyl Aromatic Compounds with Cl₂O in CCl₄

substrate	product	yield, %
		99
		89
		99
		96
		100
		97

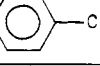
^a Reaction temperature 25 °C. ^b Reaction temperature 75 °C.

Table II. Pseudo-First-Order Rate Constants for

X--CHCl₂ + Cl₂O in CCl₄ at 25.0 °C

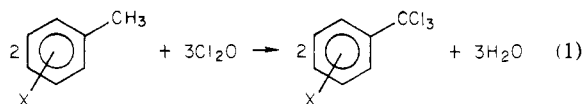
X	10 ⁴ k, s ⁻¹
NO ₂	1.05
CF ₃	1.42
Cl	2.70

Table III. Relative Rate Constants for

X--CH₃ + Cl₂O in CCl₄ at 25.0 °C

X	k _{rel}
Cl	3.44
CO ₂ CH ₃	1.76
CF ₃	2.28
NO ₂	1.00

to excessive byproducts via the ipso reaction.⁶ In marked contrast, chlorinations with Cl₂O at 25 °C can lead exclusively to trichloromethyl derivatives in high yields with water as the only byproduct (eq 1). Representative examples are shown in Table I. Mono- and dichloro products also can be produced in useful



yields by adjusting the Cl₂O/arene ratio, but the chief utility of this chemistry is the direct synthesis of relatively inaccessible, negatively substituted trichloromethyl arenes, which are convenient precursors to other functionalized arenes such as the corresponding trifluoromethyl derivatives or carboxylic acids.

In a typical reaction,^{7,8} Cl₂O (42.4 g, 0.49 mol) in CCl₄ (750

(5) We found, for example, the chlorination of *p*-nitrotoluene with excess Cl₂ at 165–170 °C for 9–14 h gave <1% *p*-nitrobenzotrichloride. Free-radical initiators or UV light had little or no effect. Catalysts such as I₂, SbI₃, C₆H₅I, C₆H₅IO, or SbCl₃ in some cases reduced the required reaction temperature to 135 °C but did not increase the yield of benzotrighloride. Other chlorinating agents including SO₂Cl₂ or *t*-BuOCl also failed to trichlorinate *p*-nitrotoluene.

(6) Traynham, J. G. *Chem. Rev.* 1979, 79, 323.

(7) Marsh, F. D. (to Du Pont) U.S. Patent 4 226 783.

(8) Solutions of Cl₂O in CCl₄ (ca. 1.0 M), prepared by passing a mixture of chlorine and air over yellow mercuric oxide,⁹ were used in this work, but in situ generation has given overall better yields for some large-scale preparations. **Caution:** Neat Cl₂O is toxic, explosive, and a strong oxidizing agent, but solutions in CCl₄ (ca. 1 M) can be handled safely and stored at -15 to 0 °C.

[†] Contribution No. 3058.

(1) (a) Balard, A. *J. Ann. Chim. Phys., Ser. 2* 1834, 57, 225. (b) Balard, A. *J. Taylor's Sci. Mem.* 1837, 1, 269. (c) Gay-Lussac, J. L. *C. R. Acad. Sci.* 1842, 14, 927.

(2) Tanner, D. D.; Nychka, N. *J. Am. Chem. Soc.* 1967, 89, 121.

(3) See, for example: Renard, J. J.; Bolker, H. I. *Chem. Rev.* 1976, 76, 487.

(4) (a) Hoch, P. E. In "Chlorine, Its Manufacture, Properties, and Uses"; Sconce, J. S., Ed.; Reinhold: New York, 1962; pp 834–863. (b) Russell, G. A. In "Free Radicals"; Kochi, J., Ed.; Wiley: New York, 1973; Vol. 1, pp 293–311. (c) Poutsma, M. L. In "Free Radicals"; Kochi, J., Ed.; Wiley: New York, 1973; Vol. 2, pp 181–185.