Journal of Organometallic Chemistry, 302 (1986) C25—C29
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

PHOTOCHEMICAL REACTIVITY OF $Os_3(CO)_{12}$ AND THERMAL ACTIVATION OF DIOSMACYCLOBUTANES TOWARDS ALKYNES

MICHAEL R. BURKE and JOSEF TAKATS*
Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2 (Canada)

(Received August 23rd, 1985)

Summary

Long wavelength photolysis of $Os_3(CO)_{12}$ and MeO_2CCCCO_2Me (DMAD) in benzene gives, as isolable products, $Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-DMAD})$ (4a) and $Os_2(CO)_6(DMAD)_4$ (5). Structural work confirms the diosmacyclobutene arrangement in 4a and reveals a unique coupling of alkynes in 5. The potentially more general thermal reaction between preformed diosmacyclobutane and alkynes gives improved yields of 4a and allows the isolation, albeit in low yield, of $Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-}CF_3CCCF_3)$ (4b).

The thermal reactivity of $Os_3(CO)_{12}$ (1), towards alkenes and alkynes has been extensively investigated and has led to a great variety of Os-containing organometallic compounds [1]. However, the photochemical behaviour of 1 towards unsaturated substrates remains a largely neglected field of research [2]. A recent report by us [3] gave evidence for facile photochemical declusterification of 1 in the presence of alkenes resulting in the unprecedented formation of saturated 1,2-diosmacyclobutanes, $Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-}CH_2CHR)$ ($R = CO_2Me$, 3a; $R = H$, 3b). Consonant with the outcome of the reaction is the involvement of an unsaturated $Os_2(CO)_8$ fragment which is rapidly scavenged by alkene [4]. In this light, it was of interest to carry out the photolysis of 1 with a variety of alkynes. At the same time, the thermal activation of compounds 3 towards alkynes was also explored as an alternate approach to unsaturated diosmacycles. The preliminary results of both studies are reported herein.

Irradiation [5] of 1 in the presence of a 15-fold excess of dimethylacetylene dicarboxylate, DMAD, results in the total consumption of 1, and the formation of a mixture of compounds. Because of separation difficulties, only two Os-containing compounds, $Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-}C(CO_2CH_3)C(CO_2CH_3))$ (4a)

0022-328X/86/$03.50

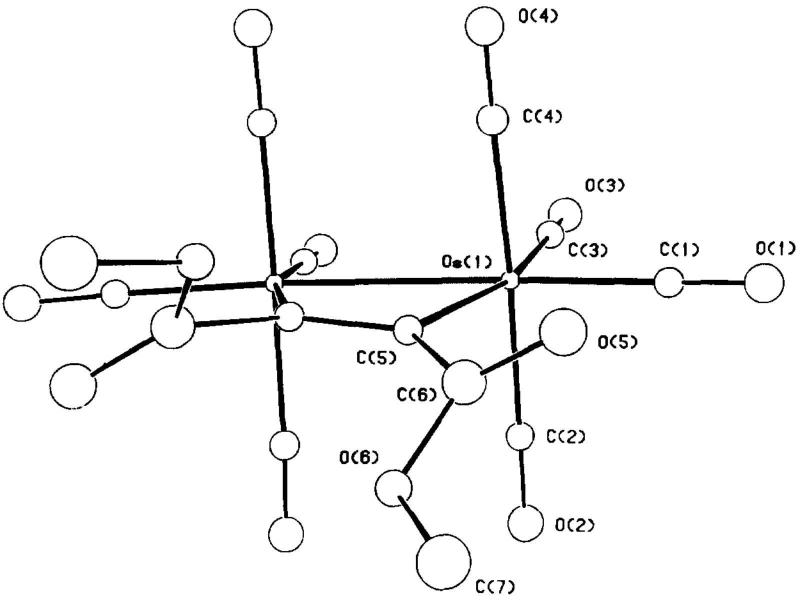

Fig. 1. Perspective view of $Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-}C(CO_2CH_3)C(CO_2CH_3))$ (4a). Atoms are represented by thermal ellipsoids at the 50% probability level. Selected bond distances (Å): Os—Os′ 2.8975(1), Os—C(5) 2.138(5), C(5)—C(5)′ 1.33(1). Selected bond angles (deg): Os—Os′—C(5) 68.3(2), Os—C(5)—C(5)′ 111.2(2). (Primed atoms are related to unmarked atoms by the two-fold symmetry axis).

and $Os_2(CO)_6(DMAD)_4$ (5), form in 10—15% yield each [6]. Spectroscopic and analytical data [7] are consistent with the formulation of 4a as the DMAD analogue of 3. An X-ray structure determination [8] confirmed the diosmacyclobutene arrangement and the results are shown in Fig. 1. The C—C bond length (1.33(1) Å) is that of a typical double bond. The Os—C(5) distances (2.138(5) Å) are single bond values [9], but are shorter than in the saturated diosmacycle, 3a [3]. Unexpectedly the Os—Os bond distance in 4a (2.8975(1) Å) is longer than that found in 3a (2.8850(5) Å), and presumably reflects the overlap requirements of the sp^2 hybridized carbon atoms, C(5) and C(5′), in 4a as compared to sp^3 hybridization in 3a. As a result, the four-membered ring in 4a is less puckered (average twist angle about Os—Os bond 6°) than in 3a (average twist angle 21°).

Although spectroscopic and analytical data on compound 5 [10] were consistent with a molecular formulation of $Os_2(CO)_6(DMAD)_4$ an unambiguous molecular structure for the compound could not be secured. X-ray quality crystals of 5 were obtained by slow evaporation of a methanol solution, and an X-ray analysis was undertaken [11]. A perspective view (Fig. 2) of the molecule reveals an unexpected arrangement of alkyne units. This arrangement can be viewed as arising from the condensation of two tricarbonylosmacyclopentadiene fragments by means of a [2+2] cycloaddition. End-on coordination of an oxygen atom from a carboxylate moiety on an adjacent osmacyclopentene ring completes the electronic requirements of each osmium center. Coordination of the carboxylate oxygen is evidenced by the lengthening of the C=O bond distance (average of 1.244(7) versus 1.189(7) Å for the unbound C=O moiety) and by the appearance of a low frequency C=O stretch-

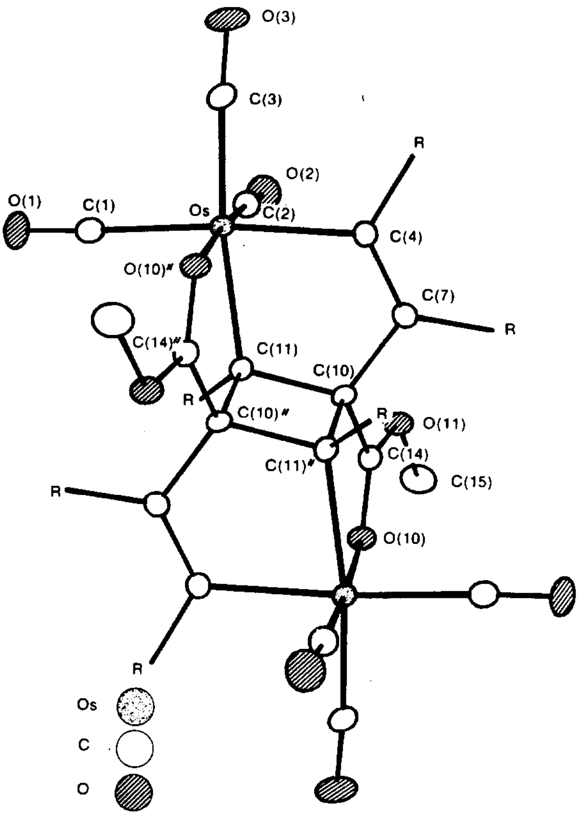

Fig. 2. Perspective view of $Os_2(CO)_6(DMAD)_4$ (5). Atoms are represented by thermal ellipsoids at the 20% probability level. For clarity some of the COOMe groups have been replaced by R. Selected average bond lengths (Å): Os—C(4) 2.101(5), Os—C(11) 2.156(5), Os—O(10)″ 2.132(5), C(14)—O(10) 1.244(7), C—O (unbound) 1.189(7), C(4)—C(7) 1.350(8), C(7)—C(10) 1.490(7), C(10—C(11) 1.578(7), C(10—C(11)″ 1.592(8). Selected average bond angles (deg): C(4)—Os—C)11) 79.8(2), C(11)—Os—O(10)″ 80.0(2), Os″—O(10)—C(14) 116.8(4), C(10)—C(11)—C(10)″ 90.7(4), C(11)—C(10)—C(11)″ 89.3(4) (″ indicates an atom centrosymmetrically related to the unprimed atom of the same name).

ing absorption at 1601 cm^{-1}. It is noteworthy that the photolysis of $Ru_3(CO)_{12}$ in the presence of DMAD gives the ruthenium analogue of 5 in 50% isolated yield [12]. No indication for the formation of diruthenacyclobutene was seen. The mode of coupling of alkynes between two metal centers giving rise to 5 appears to be unprecedented. In the work of Knox [13] and Green [14] sequential addition of alkynes to dimetallic compounds results in linear polyenyl subunits with each end attached to intact metal—metal bonded fragments.

The outcome of the photoreaction depends greatly on the nature of the alkyne. Irradiation of 1 in the presence of diphenylacetylene (DPA) gave mostly tricarbonyl(tetraphenylcyclopentadienone)osmium (6) [15], minor amounts of $Os_2(CO)_6(DPA)_2$ (7) [16] and an as yet unidentified osmium tricarbonyl containing product. The reaction of bis(trimethylsilyl)-acetylene resulted in the recovery of most of the starting materials, even after prolonged photolysis ($t > 90$ h), as did the reaction with hexafluorobutyne.

The relatively low yields in the case of DMAD and the lack of consistency with the various other alkynes in the photolyses of 1 led us to explore other synthetic routes to diosmacyclobutene complexes. Heating **3a** or **3b** to near reflux in toluene with excess DMAD results in their conversion to **4a** in 47 and 13% isolated yields, respectively [17]. The thermal reaction of **3a** with excess HFB in a Carius tube also allowed the isolation of $Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-}CF_3CCCF_3)$ [18] (**4b**), albeit in low and nonreproducible yields (isolated yields varied from almost nothing to 19% in three separate experiments). Interestingly, two isomeric tetrakis(trifluoromethyl)(carbomethoxy)cyclohexadiene tricarbonylosmium compounds are also formed in this reaction.

The scope of the thermal reaction and other more specific routes for diosmacyclobutenes are being investigated especially in view of the fact that contrary to the diosmacyclobutanes, **4a** and **4b** are thermally stable and **4a** maintains the dinuclear framework intact during carbonyl substitution [19] and presages a rich derivative chemistry.

Acknowledgement. We thank the Natural Sciences and Engineering Research Council of Canada and the University of Alberta for financial support, Dr. R. Ball for the structure determination and Johnson Matthey for generous loan of osmium tetroxide.

References

1 R.D. Adams and J.P. Selegue, in G. Wilkinson (Ed.), Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, 1982; Vol. 4, 1033—1043.

2 (a) F.A. Cotton, A.J. Deeming, P.L. Jooty, S.S. Ullah, A.J.P. Domingos, B.F.G. Johnson and J. Lewis, J. Am. Chem. Soc., 93 (1971) 4624; (b) E.G. Bryan, A.L. Burrows, B.F.G. Johnson, J. Lewis and G.M. Schiavon, J. Organomet. Chem., 129 (1977) C10; (c) S. Zobl-Ruh and W. Von Philipsborn, Helv. Chim. Acta, 63 (1980) 733.

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

4 Although different scenarios can be envisaged for the photo-declusterification of $M_3(CO)_{12}$ (M = Ru, Os) species, the involvement of an $M_2(CO)_8$ fragment at some stage in the reaction appears to be a generally accepted hypothesis; (a) R.G. Austin, P.J. Giordano and M.S. Wrighton, Adv. Chem. Ser., 1978, No 168, p. 189. (b) M.F. Desrosiers and P.C. Ford, Organometallics 1 (1982) 1715.

5 Irradiations were performed as described previously [3].

6 4 and 5 were isolated as follows: Trituration of the orange-red viscious liquid obtained upon removal of benzene in vacuo with THF gave a solid mixture of 4 and 5. The mixture was chromatographed on preparative TLC plates (SiO_2, eluent CH_2Cl_2 and 10% ethyl acetate).

7 4a: white air-stable solid; IR (CH_2Cl_2) $\nu(CO)$ 2138w, 2096s, 2050vs, ~2035sh, 2026ms, 2011 cm^{-1}, $\nu(CO_2)$ 1704w, 1693w cm^{-1}; ^1H NMR (25°C, CD_2Cl_2, 200 MHz) δ 3.66 ppm (CH_3, s). MS (125°C, 70 eV) M^+, 748 *m/e*. Anal. Found: C, 22.55; H, 0.81. $C_{14}H_6O_{12}Os_2$ calcd.: C, 22.52; H, 0.81%.

8 The structure determinations were carried out by Dr. R. Ball of the Structure Determination Laboratory of the Department of Chemistry, University of Alberta. The data were collected on an Enraf—Nonius CAD4 automated diffractometer using Mo-K_α radiation. The structure solution programs include the Enraf—Nonius Structure Determination Package by B.A. Frenz and other locally written programs. Crystal data for 4a: space group $C2/c$, $Z = 4$, a 13.211(3) Å, b 11.333(5) Å, c 11.863(2) Å, β 101.26(2)° at —50°C. In the final least-squares cycle 126 parameters were refined using 1707 observations having $I > 3.0\ \sigma(I)$. The final agreement factors were $R = 0.029$ and $R_w = 0.042$.

9 M.R. Churchill and R.A. Lashewycz, Inorg. Chem. 17 (1978) 1291.

10 5: white air-stable solid; IR (CH_2Cl_2) $\nu(CO)$ 2101s, 2033m, 2014m cm^{-1}, $\nu(CO_2)$ 1711wm, 1691wm cm^{-1}; ^1H NMR (25°C, CD_2Cl_2, 200 MHz) δ 3.48, 3.64, 3.82, 3.96, (CH_3, all s); ^{13}C NMR (25°C, CD_2Cl_2, 400 MHz) δ 198.0 (s, C(14)=O), 177.9—163.8 ppm (6s, 3C≡O + 3C=O); MS (190°C, 70 eV) M^+, 1118 *m/e* ($^{382}Os_2$). Anal. Found: C, 32.16; H, 2.17. $C_{30}H_{24}O_{22}Os_2$ calcd. C, 32.26; H, 2.23%.

11 Crystal data for 5: space group $P\bar{1}$, $Z = 2$, a 12.363(2) Å, b 14.457(3) Å, c 11.504(3) Å, α 93.71(2)°, β 115.99(2)°, γ 74.04(2)° at 25°C. In the final least-squares cycle 487 parameters were refined using 6514 observations having $I > 3.0\ \sigma(I)$. The final agreement factors were $R = 0.030$ and $R_w = 0.038$.

12 $Ru_2(CO)_6(DMAD)_4$; pale green solid; IR (CH_2Cl_2) ν(CO) 2111s, 2058m, 2036m cm^{-1}, $\nu(CO_2)$ 1723 wmbr, 1633wm cm^{-1}; ^1H NMR (25° C, CD_2Cl_2, 200 MHz) δ 3.85, 3.79, 3.70, 3.68 ppm (CH_3, all s); Anal. Found: C, 38.50; H, 2.62. $C_{30}H_{24}O_{22}Ru_2$ calcd.: C, 38.39; H, 2.58%.

13 S.A.R. Knox, R.F.D. Stansfield, F.G.A. Stone, M.J. Winter, and P. Woodward, J. Chem. Soc., Chem. Commun., (1978) 221; J. Chem. Soc., Dalton Trans., (1982) 173.

14 M. Green, N.C. Norman, and A.G. Orpen, J. Am. Chem. Soc., 103 (1981) 1269.

15 6: pale yellow air-stable solid; IR (CH_2Cl_2) ν(CO) 2083s, 2018ms, 2005m cm^{-1}; $\nu(CO_2)$ 1646wbr cm^{-1}; IR (cyclohexane) ν(CO) 2079s, 2015ms, 1997s cm^{-1}; $\nu(CO_2)$ 1677wbr cm^{-1}; ^1H NMR (25° C, $CDCl_3$ 200 MHz) δ 7.03—7.45 ppm; ^{13}C NMR (—60° C, $CDCl_3$, 200 MHz) δ 173.6 ppm (CO); mass spectrum (165° C, 70 eV) M^+ 660 *m/e*, $M^+ - n$CO (n = 1—3) (^{192}Os). Anal. Found: C, 57.91; H, 3.08. $C_{32}H_{20}O_4Os$ calcd.: C, 58.35; H, 3.06%.

16 O. Gambino, G.A. Vaglio, R.P. Ferrari, and G. Cenini, J. Organomet. Chem., 30 (1971) 381.

17 $Os_3(CO)_{12}$ is obtained in each case as a decomposition product.

18 4b: IR (CH_2Cl_2) ν(CO) 2144w, 2103s, 2055vs, ~2040sh, 2034m, 2017wm cm^{-1}; ^{13}C NMR (34° C, CD_2Cl_2, 200 MHz), δ 175.8, 171.9, 164.4 ppm (2/1/1, CO) ^{19}F NMR (25° C, CD_2Cl_2, 75.26 MHz) δ —59.3 ppm ($CFCl_3$ external reference); mass spectrum (105°C, 70 eV) M^+, 768 *m/e*, $M^+ - n$CO (n = 1—8). Anal. Found: C, 18.67; F, 14.99. $C_{12}F_6O_8Os_2$ calcd.: C, 18.80; F, 14.87%.

19 4a reacts thermally with PPh_3 to give $Os_2(CO)_4(PPh_3)_2$(DMAD); 3a gives under similar conditions $Os(CO)_4(PPh_3)$, $Os(CO)_3(PPh_3)_2$ and free methyl acrylate; M.R. Burke, unpublished observations.