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Facile Cycloreversion of Octacarbonyl-1,2-diosmacyclobutane: Convenient Source of the $Os_2(CO)_8$ Unit in the Formation of 1,2-Diosmacyclobutenes

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Cycloreversion of octacarbonyl-1,2-diosmacyclobutane, $Os_2(CO)_8(\mu\text{-}\eta^1{:}\eta^1\text{-}CH_2CH_2)$ (1), can be affected by mild thermal ($T > 28$ °C) or photochemical ($\lambda > 330$ nm) activation. In the presence of activated alkynes the reaction affords 1,2-diosmacyclobutenes in moderate to good yields, $Os_2(CO)_8(\mu\text{-}\eta^1{:}\eta^1\text{-}RCCR')$ ($R = R' = CO_2Me$ (**2a**), Ph (**2b**); $R = H$, $R' = CO_2Me$ (**2c**), C(O)Me (**2d**)). Compounds **2** have been characterized by IR and NMR spectroscopies. The ^{13}C NMR spectra indicate that the molecules are static at room temperature with regard to CO exchange processes. A detailed preparation of **1** is reported as well.

Introduction

The chemistry of dimetallacycles is of considerable current interest in view of the proven intermediacy of such species in numerous homogeneous catalytic reactions[1,2] and the pivotal role that such complexes play as models for the surface adsorption and subsequent transformation of unsaturated organic substrates.[3] Some time ago the synthesis of stable 1,2-diosmacyclobutanes was reported by Norton *et al.*[4] and by us.[5] Our methodology (eq 1) held

$$Os_3(CO)_{12} + CH_2{=}CHR \xrightarrow[C_6H_6,\ \text{room temp.}]{h\nu\ (\lambda \geq 370\ \text{nm})} Os(CO)_4(\eta^2\text{-}CH_2CHR) + \underset{1\ (R = H)}{Os_2(CO)_8(\mu\text{-}\eta^1{:}\eta^1\text{-}CH_2CHR)} \quad (1)$$

$$R = H, CO_2CH_3$$

the promise of an extensive series of 1,2-diosmacycles, accessible *via* simple photolysis of $Os_3(CO)_{12}$ in the presence of unsaturated organic ligands. Indeed, following the first report,[5] the photochemical approach was successfully used to prepare a variety of substituted 1,2-diosmacyclobutanes.[6] However, extension of the photochemical route to alkynes proved unsatisfactory. In the few instances where 1,2-diosmacyclobutenes were obtained, the yields were low and varied erratically between different preparations.[7] Application of higher intensity light in the presence of the bulky alkyne $Me_3SiC{\equiv}CSiMe_3$ led to further fragmentation and allowed the isolation of the first example of a mononuclear (alkyne)carbonylosmium complex, $Os(CO)_4(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$.[8]

Clearly a different methodology was required if the range and variety of 1,2-diosmacycles were to be extended. Such a possibility presented itself when it was discovered that the saturated 1,2-diosmacyclobutanes underwent ready cycloreversion[7] (eq 2). Elegant experiments by Norton *et al.*,[9] involving specifically labeled dideuterioethylenes, have shown that thermally induced cycloreversion and readdition reactions are stereospecific, which suggests a concerted mechanism.[10] Irrespective of the mechanistic details, the synthetic implications of eq 2 are unmistakable and we were led to consider the saturated 1,2-diosmacyclobutanes as a potential source of the $Os_2(CO)_8$ unit in further reactions with unsaturated organic substrates.

$$Os_2(CO)_8(\mu\text{-}\eta^1{:}\eta^1\text{-}CH_2CHR) \rightleftharpoons [Os_2(CO)_8] + CH_2CHR \quad (2)$$

Initial experiments[7] involved $Os_2(CO)_8(\mu\text{-}\eta^1{:}\eta^1\text{-}CH_2CHCO_2Me)$, the first easily accessible four-membered diosmacycle. When it was discovered that the unsubstituted parent compound $Os_2(CO)_8(\mu\text{-}\eta^1{:}\eta^1\text{-}CH_2CH_2)$ (1) is also available *via* photolysis, this molecule became the starting material of choice because elimination of ethylene from it is a much more facile process than that of methyl acrylate from the former complex.

Here we wish to report the thermally and/or photochemically initiated ethylene exchange reactions of **1** in the presence of activated alkynes. The method gives significant improvement in the yields of the previously described compound $Os_2(CO)_8(\mu\text{-}\eta^1{:}\eta^1\text{-}MeO_2CCCCO_2Me)$[7]

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[10] Recent matrix isolation and solution flash photolysis experiments suggest that at least the photochemical processes are more complex: (a) Haynes, A.; Paliakoff, M.; Turner, J. J.; Bender, B. R.; Norton, J. R. *J. Organomet. Chem.* **1990,** *383,* 497. (b) Grevels, F.-W.; Klotzbücher, W. E.; Seils, F.; Schaffner, K.; Takats, J. *J. Am. Chem. Soc.* **1990,** *112,* 1995.

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(**2a**), and complexes of the type $Os_2(CO)_8(\mu\text{-}\eta^1\text{:}\eta^1\text{-}RCCR')$ (R = R′ = Ph, **2b**; R = CO_2Me, R′ = H, **2c**; R = C(O)Me, R′ = H, **2d**) became accessible for the first time.

Experimental Section

All experimental procedures were performed under an atmosphere of dry nitrogen or argon using standard Schlenk techniques. Solvents were dried by refluxing with the appropriate drying agents and were distilled before use. Dimethyl acetylenedicarboxylate (DMAD), phenylacetylene, diphenylacetylene (DPA), methyl propiolate, and (trimethylsilyl)acetylene were purchased from Aldrich Chemical Co. (all minimum 99%), and 3-butyn-2-one was obtained from K and K Laboratories Inc. (minimum 99%); all were used as received. The acetone stabilizer was removed from prepurified acetylene (Matheson Gas Products) by passing the gas through a trap cooled to −78 °C. The preparation of octacarbonyl-1,2-diosmacyclobutane (1) is described below. The use of CH_2Cl_2 as reaction medium follows a suggestion made by Professor J. Norton of Colorado State University.

The photoreactions were performed in a double-walled Pyrex glass apparatus which allowed external cooling of the reaction solution, as well as that of the immersion well. The source of irradiation was a Philips HPK 125-W high-pressure mercury lamp, in conjunction with the following cutoff filters: $\lambda \geq 370$ nm, GWV (Glaswerk Wertheim); $\lambda \geq 330$ nm, uranium glass. Temperature control was maintained with a Lauda Kryomat (Model SK-65). Preparative-scale chromatographic separations were carried out on precoated TLC plates from Merck (silica gel 60 F-254, 20 cm × 20 cm × 2 mm).

^1H NMR spectra were recorded at ambient temperature on Bruker WH 200 and WP 400 spectrometers, while ^{13}C NMR data were collected on a Bruker WM300. Infrared spectra were obtained on a Nicolet MX-1 FT spectrometer over the range 2200–1600 cm^{-1}. The spectra were recorded in 0.1-mm KBr cells in alkane solutions (unless stated otherwise). The UV/vis spectrum of 1 was recorded on a Shimadzu UV-160 spectrometer. Mass spectral analyses were performed on an AEI MS-12 spectrometer operating under EI mode (70 and 16 eV). Melting points (uncorrected) were determined on a Thomas Hoover apparatus in unsealed glass capillaries. Elemental analyses were carried out by the Microanalytical Laboratory of this department.

Preparation of the Compounds. $Os_2(CO)_8(\mu\text{-}\eta^1\text{:}\eta^1\text{-}CH_2CH_2)$ (1). Dodecacarbonyltriosmium (0.500 g, 0.550 mmol), dichloromethane (200 mL), and a Teflon-coated magnetic stirring bar are placed in a 300-mL photochemical reaction vessel. A dry-ice condenser is attached to the exit port of the vessel and charged with dry ice. The suspension of $Os_3(CO)_{12}$ is vigorously stirred, and ethylene is bubbled through it for a few minutes before the light source is turned on. The light source, a high-pressure Philips HPK 125-W mercury lamp, is placed into the immersion well part of the vessel and is surrounded by a Pyrex sleeve and GWV cutoff filter ($\lambda \geq 370$ nm) tube. The Pyrex sleeve is to protect the GWV soft-glass cutoff filter from direct heat contact with the mercury lamp. The suspension is irradiated with continuous ethylene purge at 10–15 °C. As the reaction proceeds, solid $Os_3(CO)_{12}$ dissolved gradually and after 6–7 h of photolysis an almost colorless (sometimes pale straw colored), clear solution is obtained. The reaction can be monitored by IR spectroscopy, which shows characteristic bands of $Os_2(CO)_8(\mu\text{-}CH_2CH_2)$ and $Os(CO)_4(\eta^2\text{-}C_2H_4)$ at 2122 w, 2110 w, 2076 m, 2027 s, br, 2010 sh, and 1990 mbr cm^{-1}. Unfortunately the broadness of the CO stretching bands in dichloromethane and the overlapping of some of the bands do not allow identification of all the bands, nor is it possible to show conclusively the point where $Os_3(CO)_{12}$ has been completely consumed. The latter is best judged by the disappearance of the characteristic yellow coloration due to unreacted $Os_3(CO)_{12}$.

The solution is transferred to a one-neck, round-bottom flask. The volatiles (CH_2Cl_2 and $Os(CO)_4(\eta^2\text{-}C_2H_4)$) are removed at ambient temperature *in vacuo*, are collected in a clean liquid nitrogen cooled trap, and are set aside for isolation of $Os(CO)_4(\eta^2\text{-}C_2H_4)$ if this is desired. During evaporation of the solvent the solution often takes on a yellow coloration, most probably due to the presence of secondary photoproducts of the type $Os(CO)_{5-x}(C_2H_4)_x$,[11] which decompose at ambient temperature. Such behavior is more apparent when larger scale syntheses are carried out with attendant longer reaction times.

The resulting yellow, oily residue is extracted with two 30-mL portions of pentane, and the extracts are filtered through a 2-cm pad of silica gel which is further washed with 30 mL of pentane. The combined pentane solution is concentrated to *ca.* 20 mL and cooled to −20 °C overnight. Inverse filtration and drying under vacuum at ambient temperature, in the dark, gives 210 mg of off-white to pale yellow crystalline $Os_2(CO)_8(\mu\text{-}\eta^1\text{:}\eta^1\text{-}CH_2CH_2)$. Concentration of the mother liquor and crystallization give a further crop (45 mg); combined yield 73% based on the stoichiometry shown in eq 1. On the basis of numerous experiments, the yield varies between 65% and 80% for a small-scale preparation (50 mg of $Os_3(CO)_{12}$). Analytical data are as follows: IR (pentane) ν_{CO} (cm^{-1}) 2122 (w), 2077 (m), 2037 (m), 2031 (s), 2022 (m), 2010 (m), 1995 (m); ^{13}C NMR (toluene-d_8, 20 °C) δ (ppm) −25.29 (2C, C_2H_4), 169.66 (2C, CO), 172.75 (2C, CO), 180.69 (4C, CO); UV–vis (hexane) λ (nm) (ϵ, L mol^{-1} cm^{-1}) *ca.* 315 w sh (5600), 282 (9860), 270 sh (9550). Anal. Calcd for $C_{10}H_4O_8Os_2$: C, 18.99; H, 0.64. Found: C, 19.06; H, 0.57.

$Os_2(CO)_8(\mu\text{-}\eta^1\text{:}\eta^1\text{-}MeO_2CCCCO_2Me)$ (2a). (a) Thermal Route. $Os_2(CO)_8(\mu\text{-}\eta^1\text{:}\eta^1\text{-}CH_2CH_2)$ (10.0 mg, 0.016 mmol) was dissolved in 8 mL of pentane before a 100-fold molar excess of dimethyl acetylenedicarboxylate (DMAD) (0.2 mL 1.6 mmol) was added. The mixture was stirred under reduced pressure, in the dark, at 35 °C for 44 h. Solvent and most of the DMAD were stripped off *in vacuo*, and the brownish residue was redissolved in a minimum volume of acetone and this solution chromatographed on a silica gel plate with hexane/dichloromethane/acetone (6:4:1). After three consecutive cycles of elution and air drying, three well-separated zones were obtained. The first band, which was found to contain the diosmacycle **2a**, was scraped off, extracted with acetone, and evaporated to dryness. The residue was redissolved in CH_2Cl_2, dried over Na_2SO_4, and filtered. Finally the solvent was stripped off again and the pale yellow residue was dried *in vacuo*, yielding 6.0 mg (51%) of **2a**.

The second band contained the alkyne trimer hexamethyl mellitate. From the third band the mononuclear osmium complex 3 was isolated. Analytical data for 3 are as follows: IR (pentane/CH_2Cl_2, 5:1) ν_{CO} (cm^{-1}) 2106 (s), 2038 (vs) ν_{CO_2Me} (cm^{-1}) 1748 (m, br), 1732 (sh); ^1H NMR (CD_2Cl_2) δ (ppm) 3.83 (s), 3.62 (s), 3.60 (s), relative ratio of 1:1:1; mass spectrum (120 °C) *m/e* 702 (M^+ referenced to ^{192}Os), which corresponds to the molecular composition $Os(CO)_3(DMAD)_3$.

(b) Photochemical Route. $Os_2(CO)_8(\mu\text{-}\eta^1\text{:}\eta^1\text{-}CH_2CH_2)$ (10.0 mg, 0.016 mmol) and 0.2 mL of DMAD were dissolved in 8 mL of pentane, and the vessel was partially evacuated. The solution was photolyzed at ambient temperature with an external light source ($\lambda \geq 330$ nm) for 25 min. IR monitoring revealed **2a** as the only product. The workup was as described above, except that two cycles of developments were sufficient to isolate the pure sample; yield 7.5 mg (68%).

2a is an air-stable solid which melts without decomposition at 208 °C. Analytical data for this complex have been reported previously;[7] for IR and ^{13}C NMR data see Tables 1 and 2, respectively.

$Os_2(CO)_8(\mu\text{-}\eta^1\text{:}\eta^1\text{-}PhCCPh)$ (2b). (a) Thermal Route. To a solution of $Os_2(CO)_8(\mu\text{-}\eta^1\text{:}\eta^1\text{-}CH_2CH_2)$ (75.0 mg, 0.119 mmol) in 30 mL of hexane was added a 10-fold molar excess of diphenylacetylene (DPA) (211 mg, 1.18 mmol), and the mixture was stirred in the dark at 35 °C. After 15 min a pale yellow solid (which proved to be the DPA trimer, hexaphenylbenzene) began to precipitate. After 24 h the solid was separated by filtration. The clear solution was prepared for plate chromatography as described

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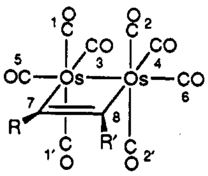
Table 1. Positions of Terminal Carbonyl Absorption Bands in 1 and 2[a]

	ν_{CO} (cm^{-1})						
1	2121 (w)	2077 (s)	2037 (m)	2030 (vs)	2021 (m)	2010 (s)	1995 (m)
2a	2135 (w)	2095 (s)	2048 (vs)	2035 (m)	2023 (m)	2017 (sh)	2008 (w)
2b	2125 (w)	2083 (s)	2046 (m)	2040 (vs)	2026 (m)	2018 (2)	2000 (w)
2c	2132 (w)	2089 (s)	2051 (sh)	2045 (vs)	2035 (m)	2021 (s)	2004 (m)
2d	2132 (w)	2088 (s)	2050 (m)	2043 (vs)	2035 (m)	2019 (s)	2004 (m)

[a] Spectra were recorded in hexane solution at ambient temperature.

Table 2. ^{13}C NMR Data for 1,2-Diosmacyclobutene Derivatives 2[a]



	chem shifts[b]					
	C(1)/C(2)[c]	C(3)/C(4)[c]	C(5)/C(6)[c]	C(7)	C(8)	$\Delta\delta_7/\Delta\delta_8$[d]
2a: R = R′ = CO_2Me	176.0	172.3	165.2	114.0	114.0	−39.4/−39.4
2b: R = R′ = Ph	178.9	173.0	167.6	113.4	113.4	−23.8/−23.8
2c: R = CO_2Me, R′ = H	177.4, 178.1	173.2, 173.6	167.1, 167.6	108.1	120.6	−33.9/−45.7
2d: R = COMe, R′ = H	177.4, 178.0	173.4, 173.8	167.7, 168.3	125.2	123.1	−43.9/−44.5

[a] The values, in ppm from TMS, were obtained in CD_2Cl_2 solution at ambient temperature. [b] Other signals: **2a**, 170.5 ($\mathit{C}O_2Me$), 51.9 ($O\mathit{C}H_3$); **2b**, C_{phenyl} at 153.7, 128.0, 127.4, 124.8; **2c**, 166.2 ($\mathit{C}O_2Me$), 51.9 ($O\mathit{C}H_3$); **2d**, 195.7 ($\mathit{C}(O)Me$), 23.3 ($C(O)\mathit{C}H_3$). [c] Individual assignment within pairs is uncertain. [d] Coordination shift: δ(alkyne) − δ(complex).

above. Four elution cycles with pentane/dichloromethane/acetone (90:9:1) finally yielded 18 mg (19%) of **2b** along with 44 mg (41%) of $Os_2(CO)_6(PhCCPh)_2$ (**4**), minor amounts of $Os_3(CO)_{12}$, and the mononuclear complex $Os(CO)_3(C_5Ph_4O)$ (**5**). Compounds **4** and **5** were identified by comparison of their characteristic IR and NMR data with those of the known compounds.[12,13]

(b) Photochemical Route. $Os_2(CO)_8(\mu\text{-}\eta^1{:}\eta^1\text{-}CH_2CH_2)$ (10.0 mg, 0.016 mmol) and 4.2 mg of DPA (0.024 mmol) were dissolved in 10 mL of pentane, and the solution was irradiated for 40 min as described above. Plate chromatography (two cycles) and workup as described above gave 4.0 mg (32%) of **2b** as a pale yellow powder melting at 146–150 °C, with decomposition. Anal. Calcd for $C_{22}H_{10}O_9Os_2$: C, 33.76; H, 1.29. Found: C, 33.96; H, 1.63. Mass spectrum (120 °C): *m/e* 784 (M^+ referenced to ^{192}Os–^{190}Os) followed by $M^+ - n(CO)$ (n = 1–8). For IR and ^{13}C NMR data, see Tables 1 and 2, respectively.

$Os_2(CO)_8(\mu\text{-}\eta^1{:}\eta^1\text{-}HCCCO_2Me)$ (2c). $Os_2(CO)_8(\mu\text{-}\eta^1{:}\eta^1\text{-}CH_2CH_2)$ (60.0 mg, 0.095 mmol) was dissolved in 5 mL of hexane to which a large molar excess of methyl propiolate (0.5 mL, 473 mmol) was added. The mixture was stirred in the dark at 35 °C for 29 h. Excess alkyne together with the solvent were stripped off *in vacuo*, and since crystallization from hexane did not allow the separation of **2c** from the catalytically formed alkyne trimer, plate chromatography was carried out with a solvent mixture of hexane/dichloromethane/acetone (33:66:1) as the eluant. The usual workup gave 46 mg (70%) of **2c** as a white powder. Crystallization from diethyl ether yielded colorless crystals melting at 120–122 °C, without decomposition. For IR and ^{13}C NMR data, see Tables 1 and 2, respectively. ^{1}H NMR (CD_2Cl_2): δ (ppm) (s, 1H, C*H*), 3.63 (s, 3H, $OC\mathit{H}_3$). Mass spectrum (175 °C): *m/e* 690 (M^+ referenced to ^{192}Os–^{190}Os); $M^+ - n(CO)$ (n = 1–8). Anal. Calcd for $C_{12}H_4O_{10}Os_2$: C, 20.93; H, 0.59. Found: C, 20.94; H, 0.52.

$Os_2(CO)_8(\mu\text{-}\eta^1{:}\eta^1\text{-}HCCC(O)Me)$ (2d). $Os_2(CO)_8(\mu\text{-}\eta^1{:}\eta^1\text{-}CH_2CH_2)$ (52.0 mg, 0.082 mmol) was dispersed in 0.5 mL of 3-butyn-2-one; the vessel was partially evacuated and heated to 60 °C in the dark. After 4 h the reaction mixture was diluted with 30 mL of hexane. The mixture was filtered, and the brown precipitate thus obtained was washed with some additional hexane. The combined solutions were first evaporated to dryness, and the residue was then redissolved in hexane. Cooling to −78 °C gave 47 mg of **2d** (86%) slightly contaminated with traces of the alkyne trimer 1,3,5-tris(acetyl)benzene. A final recrystallization from CD_2Cl_2 gave analytically pure, colorless crystals of **2d**, which started to decompose at 160 °C before melting could be observed. For IR and ^{13}C NMR, see Tables 1 and 2, respectively. ^{1}H NMR (CD_2Cl_2): δ (ppm) 8.54 (s, 1H, C*H*), 2.19 (s, 3H, $C(O)C\mathit{H}_3$). Mass spectrum (110 °C): *m/e* 674 (M^+ referenced to ^{192}Os–^{190}Os), $M^+ - n(CO) - m(COMe)$ (n = 1–8, m = 0, 1). Anal. Calcd for $C_{12}H_4O_9Os_2$: C, 21.43; H, 0.60. Found: C, 21.48; H, 0.60.

Some Unsuccessful Attempts. Reactions with Acetylene. Heating compound **1** at 34 °C under an acetylene purge gave a mixture of products, from which only $Os_3(CO)_{12}$ could be isolated and identified.

Photolysis of **1** at −55 °C under an acetylene purge also resulted in a mixture of products. $Os_3(CO)_{12}$ appeared not to form under these conditions. Attempts to separate the mixture failed. Low-temperature sublimation and fractional crystallization gave small amounts of two of the components in somewhat impure state. The IR spectra showed that these were $Os(CO)_4(\eta^2\text{-}HC{\equiv}CH)$ and $Os_2(CO)_8(\mu\text{-}\eta^1{:}\eta^1\text{-}HCCH)$.[14]

Reactions with Phenylacetylene. Photolysis of **1** at room temperature in pentane in the presence of a large excess of phenylacetylene led to consumption of the starting material. The IR spectrum showed formation of $Os(CO)_5$ (major product) and a small amount of $Os_3(CO)_{12}$ with perhaps a hint of $Os_2(CO)_8(\mu\text{-}\eta^1{:}\eta^1\text{-}HCCPh)$. There was also catalytic formation of 1,3,5-triphenylbenzene.

Reactions with (Trimethylsilyl)acetylene. Photolysis of **1** at 0 °C in pentane in the presence of excess (trimethylsilyl)acetylene led to the consumption of the starting material. The IR spectrum of the crude reaction mixture showed the formation of two major components: a tetracarbonyl species, perhaps $Os(CO)_4(\eta^2\text{-}HCCSiMe_3)$, and a tricarbonyl compound of unknown composition. Attempted separation and isolation of pure components failed.

Results and Discussion

Synthesis. (a) Thermal Exchange Reactions. Initial attempts to prepare alkyne-bridged diosmium com-

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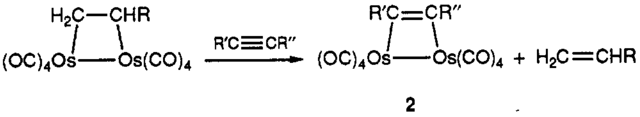
Scheme 1



plexes of the general type **2** *via* photolysis of $Os_3(CO)_{12}$ in the presence of alkynes met with little success.[7,8] As an alternate synthetic route the possibility of exchanging the alkene bridge in saturated 1,2-diosmacyclobutanes by alkynes was investigated (Scheme 1). The first reactions[7] involved $Os_2(CO)_8(\mu\text{-}\eta^1{:}\eta^1\text{-}CH_2CHCO_2Me)$. Although the results were encouraging, in the sense that with dimethyl acetylenedicarboxylate reasonable yields of $Os_2(CO)_8(\mu\text{-}\eta^1{:}\eta^1\text{-}MeO_2CCCCO_2Me)$ (**2a**) were obtained, the relatively high temperature ($T \geq 80$ °C) required to effect the exchange of methyl acrylate was disappointing, since it indicated that only thermally robust diosmacycles could ever be synthesized from the above complex. With the availability of the unsubstituted octacarbonyl-1,2-diosmacyclobutane (**1**) in synthetically useful quantities *via* the photochemical route, our attention turned to this material in anticipation that ethylene elimination from **1** would facilitate the task of generating the reactive $Os_2(CO)_8$ unit.

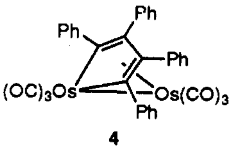
Different alkynes were added to hexane solutions of **1** and stirred in the dark. As IR monitoring did not show any conversion at room temperature after several hours, the mixtures were carefully warmed. Independent of the nature of the alkynes, reaction started at about 28 °C in every case, indicating the onset of ethylene elimination from **1**. A similar temperature was observed by Norton *et al.*[9] in their study of the mechanism of thermal extrusion of ethylene from **1**. The yield of products varied with the nature and excess of the alkyne used (eq 3).

$$Os_2(CO)_8(\mu\text{-}\eta^1{:}\eta^1\text{-}CH_2CH_2) + RC{\equiv}CR' \xrightarrow[\text{alkane}]{\Delta} \underset{\textbf{2a–d}}{Os_2(CO)_8(\mu\text{-}\eta^1{:}\eta^1\text{-}RCCR')} + C_2H_4 \quad (3)$$

2a, R = R' = CO_2Me (51%); **2b**, R = R' = Ph (19%); **2c**, R = CO_2Me, R' = H (70%); **2d**, R = C(O)Me, R' = H (86%)

The reactions with π-acidic alkynes, such as dimethyl acetylenedicarboxylate (DMDA), methyl propiolate, and but-3-yn-2-one gave the respective 1,2-diosmacyclobutene derivatives **2a**, **2c**, and **2d** in satisfactory to high yields. The best yield was obtained when **1** was heated in neat but-3-yn-2-one for a short time (4 h) at 60 °C.

The reaction with diphenylacetylene (DPA) resulted in a significantly lower yield of **2b**, and this is most likely a reflection of the poorer π-acidity of DPA compared to the other alkynes. In addition to **2b**, the major byproduct of this reaction was the flyover complex $Os_2(CO)_6(\mu\text{-}C_4Ph_4)$ (**4**) and small amounts of $Os(CO)_3(\eta^4$-tetraphenylcyclopentadienone) (**5**). These were identified by comparison of their spectroscopic data with published values.[12,13]



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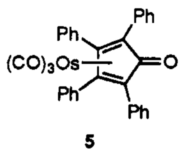

5

The formation of **2a** was also accompanied by cleavage of the Os–Os bond, leading to the mononuclear species **3**. This bright yellow compound is almost insoluble in alkanes. Mass spectral analysis and the ^{1}H NMR spectrum suggest a molecular composition of $Os(CO)_3(DMAD)_3$. The IR spectrum shows two CO stretching bands in the region associated with terminal carbonyl groups with an intensity ratio typical for *fac* metal tricarbonyl species.[15] Although reasonable postulates can be made, an unambiguous molecular structure cannot be deduced from the simple spectroscopic data.

$Os_3(CO)_{12}$ was also found as a byproduct in every thermal reaction, the amount increasing with decreasing concentration of the alkyne ligand. Usually the amount of $Os_3(CO)_{12}$ formed was small, except in the thermal reaction with acetylene, where it was the major and only isolable product (see Experimental Section).

The reactions leading to **2** were also accompanied by formation of the respective alkyne trimers $C_6R_3R'_3$. They are formed catalytically, and their overall yields are strongly dependent on the excess of free alkyne. Formation of the alkyne trimers started as soon as the temperature of the reaction mixtures exceeded that necessary for the liberation of ethylene from **1**. They were identified by NMR and mass spectral analyses, and as a matter of interest, it was found that in cases of R ≠ R' only those benzene derivatives were formed which are symmetrically substituted in positions 1, 3, and 5. Although it is tempting to involve an Os_2 complex, presumably in the form of $Os_2(CO)_8$, in this catalytic cycle, the formation of some $Os_3(CO)_{12}$ in all the experiments could also implicate a mononuclear compound as well. It is well-known that there are both mono- and dinuclear species which are effective catalysts for alkyne trimerization processes.[16]

(b) Photochemical Exchange Reactions. Investigations of the photochemical behavior of **1** led to the observation that the bridging ethylene unit could also be eliminated below 28 °C while the $Os_2(CO)_8$ unit was retained. This proved to be a useful synthetic alternative to the thermal route for the preparation of diosmacyclobutene derivatives. As there is a wavelength-dependent competition between ethylene photoelimination and cleavage of the Os–Os bond, the best results were obtained by irradiation through a uranium cutoff filter glass ($\lambda \geq 330$ nm) in the presence of a large excess of alkynes. Octacarbonyldiosmacyclobutane (**1**) exhibits a shoulder in its absorption spectrum at 330 nm, but the nature of this transition is presently not known.

This variation improved the yields of crystallized **2a** and **2b** to 68% and 32%, respectively. The mild conditions of the photoexchange process also allowed us for the first time to observe the formation of the parent diosmacyclobutene, **2e** (eq 4). The reaction is accompanied by the formation of several other products, including $Os(CO)_4(\eta^2\text{-}HCCH)$, and **2e** could not be isolated in a pure form via this approach. However, the observation of the last two compounds was in no small measure responsible for our discovery that condensation of $Os(CO)_4(\eta^2\text{-}HCCH)$ with $Os(CO)_5$ provides a convenient and high-yield synthesis of **2e**.[14]

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(15) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: London, 1975.

(16) (a) Keim, W.; Behr, A.; Röper, M. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: London, 1982; Vol. 8, pp 410–413. (b) Green, M.; Kale, P. A.; Mercer, R. J. *J. Chem. Soc., Chem. Commun.* **1987**, 375 and references therein.

$$\underset{1}{Os_2(CO)_8(\mu\text{-}\eta^1{:}\eta^1\text{-}CH_2CH_2)} + C_2H_2 \xrightarrow[T \le -50\ ^\circ C]{h\nu(\lambda \ge 330\ nm)} \underset{2e}{Os_2(CO)_8(\mu\text{-}\eta^1{:}\eta^1\text{-}HCCH)} + Os(CO)_4(\eta^2\text{-}HCCH) + \text{other products} \qquad (4)$$

Unfortunately the photochemical exchange reaction is not universally applicable either. In reactions employing only mildly activated (PhC≡CH) or bulky ($Me_3SiC{\equiv}CH$) alkynes Os–Os bond cleavage dominated over simple alkyne addition to the nascent $Os_2(CO)_8$ unit and led to various mononuclear species. Instead of $Os_3(CO)_{12}$, $Os(CO)_5$ was detected as a byproduct in these photoreactions. With phenylacetylene catalytic formation of 1,3,5-triphenylbenzene was also observed.

Spectroscopic Characterization. Complexes **2a–d** all showed parent molecular ions (M^+) in their mass spectra. These were accompanied by fragments primarily arising from loss of up to eight carbonyl groups, as could be excpected for complexes containing the $Os_2(CO)_8$ subunit. Loss of the bridging alkyne did not occur *prior* to loss of all eight terminal carbonyl groups, a testimony to the robustness of the central diosmacyclobutene ring.

The IR spectra of complexes **2**, just like that of **1**, show seven distinct bands in the terminal carbonyl stretching region (Table 1). The similar patterns support the conclusion that the molecular structures of the two classes of compounds are analogous. The correct diosmacyclobutene formulation was corroborated by an X-ray structure analysis of **2a**.[7] For convenience and ease of visualization, a diagram of **2a** is shown in Figure 1. Since the low molecular symmetry, C_2 for **2a** and **2b** and C_1 for **2c** and **2d**, renders all eight carbonyl stretching vibrations symmetry allowed, the absence of the eighth band either is due to accidental overlap of two bands or perhaps indicates that local C_{2v} symmetry is a valid approximation for the center core of these diosmacycles. Indeed, under C_{2v} symmetry seven bands are expected, namely $3A_1$, $3B_1$, and B_2. The difference in π-acidity of the bridging alkynes is nicely reflected by the positions of the carbonyl absorption bands, the frequency ordering being **2a** > **2c** ≈ **2d** > **2b**. On the other hand, the small difference in the net electronic properties between the two acceptor moieties in the monosubstituted complexes **2c** and **2d** is corroborated by their nearly identical IR spectra. The C═O vibrational bands of the organic moieties in **2a**, **2c**, and **2d** are observed between 1700 and 1710 cm^{-1}. In the unsymmetrically substituted compounds **2c** and **2d**, weak bands at 1695 and 1657 cm^{-1}, respectively, are also seen. These are assigned to the asymmetric C═C stretching vibrations of the bridging alkyne unit. Apparently these bands are too weak to be observed in the other two complexes containing symmetrically substituted alkynes.

^{13}C NMR data for the alkyne-bridged diosmacycles are compiled in Table 2, and Figure 2 displays an APT ^{13}C NMR spectrum[17] for complex **2b**. All spectra show sets of sharp signals at room temperature, consistent with static molecules with regard to CO site exchange processes. Assignment of the eight carbonyl ligands is based on relative intensities as well as comparison with analogous complexes of the type $MM'(CO)_8(\mu\text{-}\eta^1{:}\eta^1\text{-}RCCR)$ (MM′ = Ru; M = Ru, M′ = Os; R = CF_3).[18]

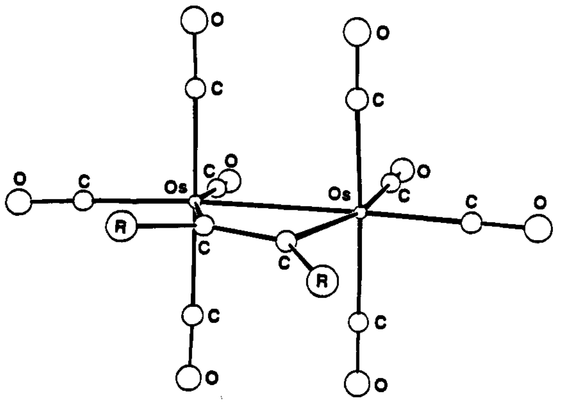

Figure 1. Schematic diagram of the molecular structure of $Os_2(CO)_8(\mu\text{-}\eta^1{:}\eta^1\text{-}DMAD)$; R = CO_2Me.

As seen in Figure 2 and Table 2, the number and relative intensity of the osmium-bound carbonyl group signals imply a real or apparent mirror plane of symmetry for compounds **2**, containing the central Os_2C_2 ring and the radial carbonyl ligands. In the solid state the four-membered ring in **2a** is not planar but puckered (Figure 1), with an average twist angle of 8°. Yet, conformational mobility of the diosmacyclobutene ring in solution is expected to be great. Indeed, in the related saturated octacarbonyl-1,2-diosmacyclobutane (**1**), with a much more severe ring puckering (Os–C–C–Os torsion angle is 32.5°),[6e] ring inversion is still rapid on the NMR time scale down to −90 °C.[4] Thus, the mirror plane seen in the ^{13}C NMR spectra of complexes **2** is a result of time averaging due to rapid conformational changes of the slightly puckered diosmacyclobutene ring.

Clearly the NMR signals, with a relative intensity of 2, can be assigned to the carbonyl groups 1 and 2 (see Table 2 for numbering). Discrimination between carbonyl ligands 3/4 and 5/6, *trans* and *cis* to the bridging alkyne unit, is made possible by comparison to related diruthenacyclobutenes, where they exhibit different fluxional behavior. For instance, in $Ru_2(CO)_8(\mu\text{-}\eta^1{:}\eta^1\text{-}CF_3CCCF_3)$[18] carbonyl groups 1, 2, 6, 2′, 1′, and 5 undergo ready exchange *via* the well-known "merry-go-round process",[19] which permutes CO groups that are restricted to a common plane. The carbonyl groups 3 and 4, which are orthogonal to this plane, do not take part in the exchange. On this basis, unambiguous assignment of carbonyl ligands 3/4 and 5/6 is obtained in the diruthenium complex. By analogy, assuming that the trend in chemical shifts is transferable to the osmium complexes, the lower field signals are assigned to carbonyls 3/4 and the remaining signals to carbonyls 5/6. In the asymmetric alkyne-bridged compounds **2c** and **2d**, distinct resonances are seen for these ligands. In the absence of a reliable handle, the assignment to individual carbonyl groups in these pairs is not possible.

Differences in chemical shifts of the corresponding CO groups in complexes **2a–d** are small but significant. The chemical shift moves to lower field with decreasing π-acidity of the bridging alkyne unit due to strong $d_\pi(Os) \rightarrow p_{\pi^*}(CO)$ back-donation. The shift to lower field with increasing metal-to-carbonyl back-donation is well documented in metal carbonyl chemistry.[20]

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[17] APT = Attached Proton Test; for details, see: Brown, D. W.; Nakashima, T. T.; Rabenstein, D. L. *J. Magn. Reson.* **1981**, *45*, 302.

[18] Gagné, M. R.; Takats, J. *Organometallics* **1988**, *7*, 561.

[19] Bond, E.; Muetterties, E. L. *Chem. Rev.* **1978**, *78*, 639.

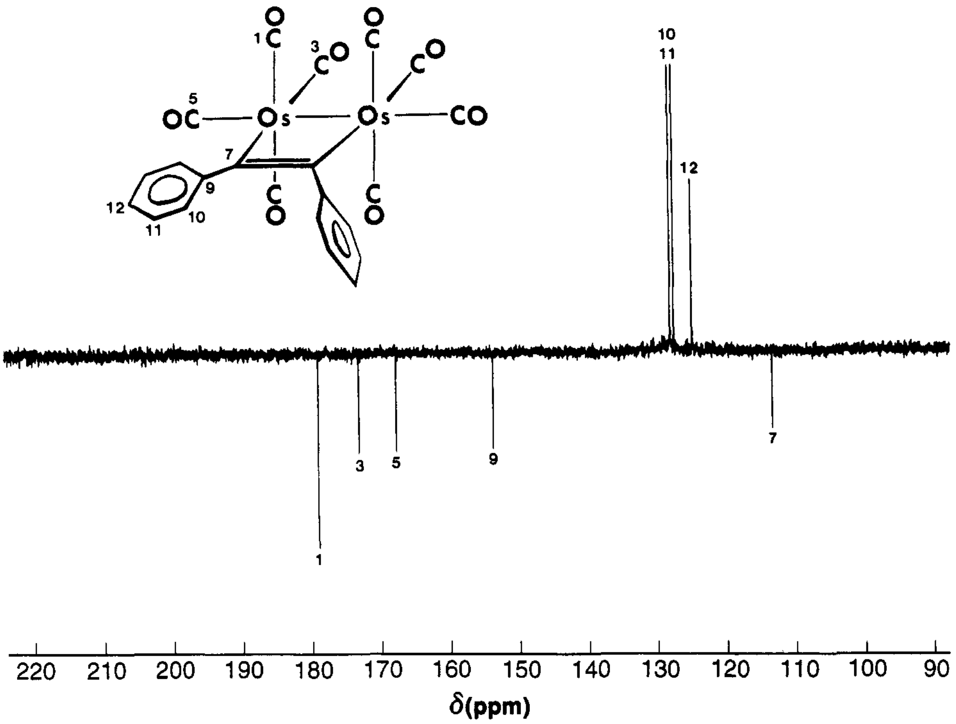

Figure 2. APT ^{13}C NMR spectrum of $Os_2(\mu\text{-}\eta^1:\eta^1\text{-}PhC{\equiv}CPh)$ (for numbering see Table 2).

The resonance signals of the formerly sp-hybridized alkyne carbon atoms C(7) and C(8) exhibit coordination shifts ($\Delta\delta$) to lower field due to their increased sp^2 character, although the shifts are modulated by the strong shielding effect of the metal atoms. Thus, the acceptor-substituted complexes **2a**, **2c**, and **2d** undergo an average downfield shift of *ca.* 40 ppm, whereas **2b** experiences a shift of only about half this amount, 23.8 ppm. This is most likely caused by a smaller anisotropic effect of the phenyl groups on the alkyne carbon resonance in the free alkyne rather than a much different bonding situation in diosmacycle **2b**. Steric hindrance is expected to hamper conjugation of the central C=C double bond with its substituents in every case and thus cannot account for the difference in coordinated shift between **2a**, **2c**, **2d** and **2b**.

The individual assignment of positions C(7) and C(8) in **2c** and **2d** is based on the different amount of NOE enhancements these signals are expected to show in their proton-decoupled ^{13}C NMR spectra. Due to the strong proton coupling, the higher intensity signals in **2c** and **2d** are assigned to C(8), the carbon bearing a hydrogen atom. This assignment is supported by a simplified application of an increment system,[21] which allows an estimation of the ^{13}C chemical shifts of disubstituted olefins.

Conclusions

Facile cycloreversions of ethylene from 1,2-diosmacyclobutane, initiated by mild thermal or photolytic activation, generate the reactive $Os_2(CO)_8$ unit. Although this species adds to the triple bond of substituted alkynes to form the respective 1,2-diosmacyclobutenes, the proccedure appears to be restricted to unsaturated substrates activated by electron-withdrawing substituents. Insufficient alkyne activation leads to increased formation of binary osmium carbonyls, namely $Os_3(CO)_{12}$ *via* the thermal route or $Os(CO)_5$ *via* the photochemical process. From these observations it can be concluded that $Os_2(CO)_8$ possesses a considerable lifetime, which allows clusterification or dissociation, even in the presence of large excesses of alkyne. Indeed, the species has been detected and characterized by matrix isolation[10a] and solution flash photolysis[10b] experiments.

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Note Added in Proof. Synthesis of 1: For a description of the photochemical apparatus see: Grevels, F.-W.; Reuvers, J. G. A.; Takats, J. *Inorg. Synth.* **1986**, *24*, 176. For a slightly different approach, utilizing aqueous $NaNO_2$ instead of GWV glass as filter, see: Norton, J. R.; et al. *Organometallics* **1991**, *10*, 3145.

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