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SYNTHESIS AND REACTIVITY OF 1,2-DIOSMACYCLES

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Abstract—Photolysis of $Os_3(CO)_{12}$ in the presence of alkenes with filtered radiation ($\lambda >$ 370 nm) leads to fragmentation of the cluster and gives mononuclear $Os(CO)_4(\eta^2\text{-alkene})$ derivatives and dinuclear 1,2-diosmacyclobutanes, $Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-CHRCHR'})$. Attempts to extend the photochemical method to the preparation of other types of diosmacycles met with little success. As an alternative synthetic approach the exchange of ethylene in $Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-}C_2H_4)$, **3a**, for other unsaturated organic substrates was explored. Reaction of **3a** with alkynes gave diosmacyclobutenes, whereas with dienes regiospecific 1,2-addition was observed. The scope and limitations of the exchange reactions are reviewed. The properties of the diosmacycles and of the product obtained via hydride abstraction from **3a** are outlined.

Interest in the chemistry of dimetallacycles can be traced to the now often verified postulate that such species are involved as key intermediates in a variety of chemical reactions and that they may serve as useful models for the bonding and transformation of unsaturated organic substrates on metal surfaces.[1] Although the importance of these compounds is well recognized, the number of examples, with the exception of dimetallacyclopropanes[2] (i.e. alkylidene bridged dimetallic complexes) and those resulting from alkyne addition to dimetallic complexes,[3] is still rather small.

It is the purpose of this article to give a brief overview of our discovery, albeit serendipitous, of a convenient photochemical synthesis of 1,2-diosmacyclobutanes[4] and the utilization of these compounds for the preparation of other diosmacycles. Emphasis will be on the work from the author's laboratory, although relevant work from other groups will be also mentioned.

PHOTOCHEMICAL SYNTHESIS OF 1,2-DIOSMACYCLOBUTANES, $Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-CHRCHR'})$

The successful preparation of a range of $Ru(CO)_4(\eta^2\text{-alkene})$ compounds via photolysis of $Ru_3(CO)_{12}$ (**1–Ru**) in the presence of alkenes[5] [eq. (1)] prompted us to investigate the similar photoreaction with $Os_3(CO)_{12}$(**1–Os**).

$$Ru_3(CO)_{12} + \text{alkene} \xrightarrow[\text{hydrocarbon, RT}]{h\nu,\,\lambda > 370\,\text{nm}} 3Ru(CO)_4(\eta^2\text{-alkene}). \quad (1)$$

The goal being to complete the series of iron triad $M(CO)_4(\eta^2\text{-alkene})$ (M = Fe, Ru, Os) compounds and compare their properties.

However a potential problem presented itself. It was well documented at the time, that whereas near-UV irradiation of $Ru_3(CO)_{12}$ in the presence of CO, C_2H_4 and PPh_3 led to photofragmentation,[6] the reaction between $Os_3(CO)_{12}$ and PPh_3 resulted in photosubstitution.[7] Indeed the success of the reaction shown in eq. (1) resides in the use of selective excitation into the first allowed electronic band of $Ru_3(CO)_{12}$ at 380 nm, which is known to have $\sigma \rightarrow \sigma^*$ (Ru—Ru) character and therefore leads to facile and synthetically efficient photofragmentation.† The different reactivity of $Os_3(CO)_{12}$ was attributed to a reversal in the relative order of the two lowest energy absorptions. In the case of osmium, the predominantly $\sigma \rightarrow \sigma^*$ (Os—Os) transition being associated with the second band at 330 nm. Accordingly, the first synthetic reactions with $Os_3(CO)_{12}$ utilized Pyrex filtered radiation ($\lambda >$ 280 nm) to ensure excitation into the $\sigma \rightarrow \sigma^*$ transition. A π-acidic alkene, methyl acrylate, was chosen as the organic substrate in order to favour the formation

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† Reaction (1) proceeds in 100% yield by IR spectroscopy. Isolated yields are somewhat lower and depend on the nature of the ligand, the most stable compounds are obtained with strongly π-acidic alkenes.

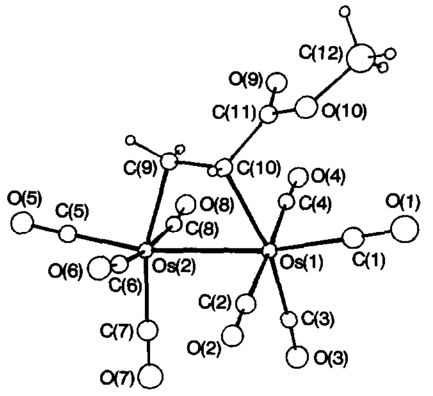

Fig. 1. Molecular structure of $Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-}CH_2CHCO_2CH_3)$,[9] **3b**. Relevant bond distances (Å): Os(1)—Os(2) = 2.8850(1), Os(1)—C(10) = 2.223(9), Os(2)—C(9) = 2.203(9), C(9)—C(10) = 1.52(1). Torsional angle Os—Os and C—C 23.0°.

of a stable product. Although $Os_3(CO)_{12}$ was consumed, mixtures of carbonyl–alkene complexes were obtained which defied separation and characterization. Undaunted, if a bit sceptical, the same reaction was tried with near-UV radiation. Serendipity smiled and formation of carbonyl–alkene complexes of osmium was again observed.† After some initial difficulties, it was ascertained[9] that the crude reaction product was in fact a mixture of two compounds [eq. (2)], the anticipated monomeric **2b** and the unexpected diosmacyclobutane derivative **3b**, Fig. 1.

$$Os_3(CO)_{12} + CH_2CHCO_2CH_3 \xrightarrow[\text{benzene, 15°C}]{h\nu,\, \lambda > 370\,\text{nm}} \underset{\mathbf{2b}}{Os(CO)_4(\eta^2\text{-}CH_2CHCO_2CH_3)} + \underset{\mathbf{3b}}{Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-}CH_2CHCO_2CH_3)}. \quad (2)$$

While this work was in progress we have learned that Norton and co-workers[10] have synthesized the unsubstituted 1,2-diosmacyclobutane, **3a**, via a very different reaction sequence [eq. (3)]. Prompted by the successful preparation of **3a** without the stabilizing electron withdrawing substituents on carbon, the photoreaction under a continuous ethylene purge was carried out and, gratifyingly, gave a mixture of $Os(CO)_4(\eta^2\text{-}C_2H_4)$, **2a** and **3a**.

$$Os_3(CO)_{12} \rightarrow Na_2[Os_2(CO)_8]$$

$$Na_2[Os_2(CO)_8] + TsOCH_2CH_2OTs \rightarrow \underset{\mathbf{3a}}{Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-}C_2H_4)}. \quad (3)$$

Since **2a** is volatile and consequently removed during the evaporation of the solvent, the isolation of **3a** is very simple‡ and makes the photochemical route the preparative method of choice[11] for this interesting and synthetically very useful material. Extension of this method to other olefins has met with moderate success. In our hands,[12] substituted diosmacyclobutanes were observed with propylene, methylvinyl ketone, dimethylfumerate (DMF) and dimethyl maleate (DMM). Other workers reported similar results with 1-octene,[13] 5,6-dimethylidene-7-oxabicyclo[2.2.1]-hept-2-ene[14] and propylene, 1-butene, styrene, tert-butylethylene.[15]

The molecules exhibit relatively rich IR spectra in the terminal carbonyl region with a characteristic absorption above 2100 cm^{-1}. Another typical feature is the high field position of the carbon atoms of the Os_2C_2 ring in the ^{13}C NMR spectrum (cf. **3a**, $\delta_C = -25.2$ ppm). The stability of the diosmacyclobutanes is a function of both steric and electronic factors. Thus the propylene bridged compound is much less stable than **3a** which in turn is less stable than **3b** and other diosmacyclobutanes having electron withdrawing substituents at the bridgehead carbon atoms. Although the reaction with π-acidic alkenes is not always without complication, nor does it guarantee the universal formation of dimetallacyclic compounds. For instance, the photoreaction with DMM proceeded with isomerization of the alkene and formation of all possible mono- and dinuclear compounds [eq. (4)]. Contrary to this, the reaction with **1–Ru** gave only $Ru(CO)_4(\eta^2\text{-DMM})$.[5]

$$Os_3(CO)_{12} + DMM \xrightarrow[\text{benzene, 15°C}]{h\nu,\, \lambda > 370\,\text{nm}} Os(CO)_4(\eta^2\text{-DMM}) + Os(CO)_4(\eta^2\text{-DMF}) + \underset{\mathbf{3c}}{Os_2(CO)_8(\mu\text{-DMM})} + \underset{\mathbf{3d}}{Os_2(CO)_8(\mu\text{-DMF})}. \quad (4)$$

The structures of **3c** and **3d**, shown in Figure 2, also emphasize another characteristic of the com-

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† From a recent study by Bensten and Wrighton,[8] it is clear that severe overlap of the absorption bands at room temperature is the cause of the early difficulties and for the success of the filtered radiation approach. In other words irradiation with λ > 370 nm gives suitable excitation into the tail-end of the σ → σ* band without affecting the higher energy band which, under Pyrex filtered radiation is also excited and causes further reaction of the primary photoproducts.

‡ Yields of up to 86% based on the presumed stoichiometry of eq. (2) (57% based on osmium carbonyl) have been achieved. The average yield of several synthetic runs (0.5 g of $Os_3(CO)_{12}$) is approximately 45% based on osmium.

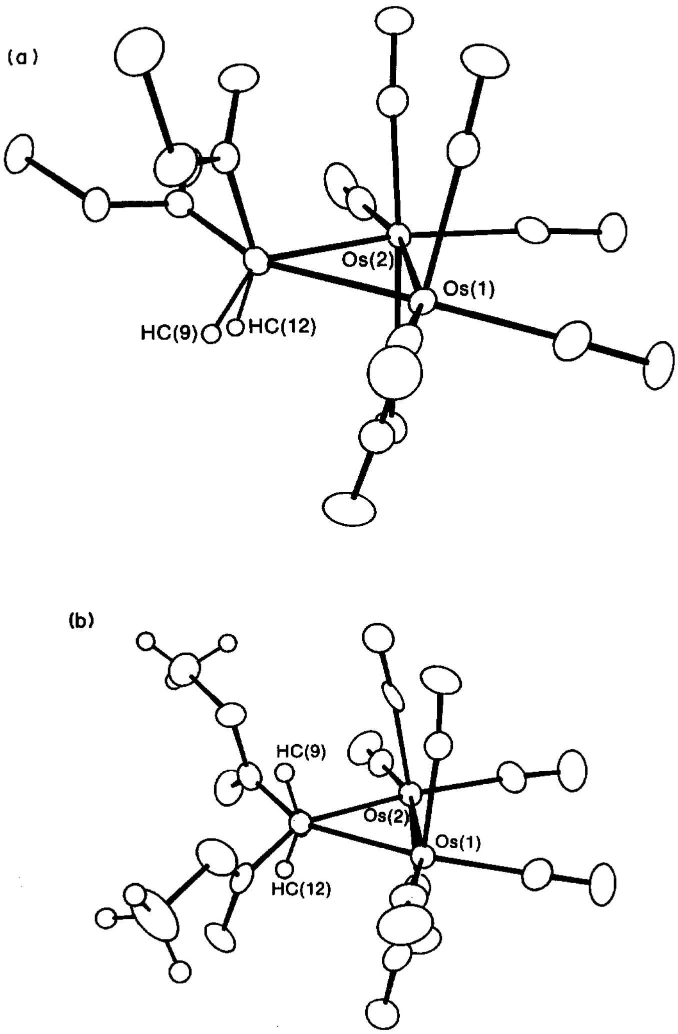


Fig. 2. Views of (a) $Os_2(CO)_8(\mu$-DMM), **3c**, and (b) $Os_2(CO)_8(\mu$-DMF), **3d**, looking down the C(9)—C(12) vector.[12] Relevant bond distances (Å) **3c**: Os(1)—Os(2) = 2.8788(4), Os(1)—C(9) = 2.220(7), Os(2)—C(12) = 2.202(6), C(9)—C(12) = 1.54(1); **3d**: Os(1)—Os(2) = 2.8719(4), Os(1)—C(9) = 2.205(6), Os(2)—C(12) = 2.221(7), C(9)—C(12) = 1.501(9). Torsional angle Os—Os and C—C: **3c** 18.5°; **3d** 23.2°.

pounds, the puckered nature of the four-membered ring. However, the conformational mobility of the ring is high.

No reaction between **1–Os** and tetrafluoroethylene, perfluoro-2-butene and maleic anhydride was observed, although a diosmacyclobutane based on the latter π-acidic olefin is available via an alternate route (see below).

Thus it appears, at least to this author, that even after several thoughtful reports, all the details of the photofragmentation of **1–Os**[8,13] and **1–Ru**[16] are still not completely understood. What seems irrefutable is that at some stage $M_3(CO)_{12}$ (M = Fe, Ru, Os) breaks down to mononuclear, $M(CO)_4$ and dinuclear, $M_2(CO)_8$ fragments probably stabilized by some supportive ligands. Based on this consideration it was of interest to establish whether the interception of the dinuclear osmium fragment by other unsaturated organic substrates may lead to a potentially general synthetic strategy for a variety of diosmacyclic compounds.

PHOTOREACTION OF $Os_3(CO)_{12}$ WITH ALKYNES

Although the thermal reaction of **1–Os** with alkynes has resulted in a rich derivative chemistry,[17] the corresponding photoreaction remained, surprisingly, untouched. With the precedent established by the saturated 1,2-diosmacyclobutanes, the

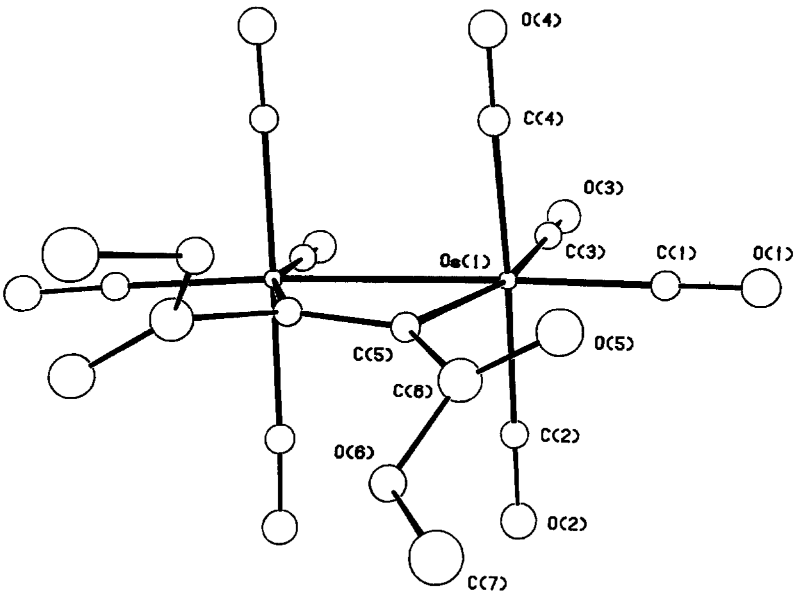


Fig. 3. Molecular structure of $Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-DMAD})$,[19] **4–Os**. Relevant bond distances (Å): Os(1)—Os(1) = 2.8975(1), Os(1)—C(5) = 2.138(5); C(5)—C(5)′ = 1.33(1). Torsional angle Os—Os and C—C 8.4°.

less common "parallel" bonding mode of the alkyne[18] (i.e. formation of 1,2-diosmacyclobutene) was anticipated from the photoreaction.

Since activated alkenes afforded the most stable diosmacyclobutanes, the choice of dimethylacetylenedicarboxylate (DMAD, $C_2(CO_2CH_3)_2$) was obvious. Unfortunately the reaction resulted in the formation of a mixture of products [eq. (5)].

$$Os_3(CO)_{12} + DMAD \xrightarrow[\text{benzene, RT}]{h\nu > 370\,\text{nm}}$$

$$Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-DMAD})$$

4–Os

$$+ Os_2(CO)_6(DMAD)_4 + C_6(CO_2CH_3)_6$$

5–Os

$$+ \text{unidentified compound(s)}. \qquad (5)$$

Because of separation difficulties only two osmium containing products could be isolated, in low yields.[19] Compound **4–Os** is the desired 1,2-diosmacyclobutene, Fig. 3. As expected from the more rigid parallel alkyne bridge, the four membered ring in **4–Os** is less puckered than in the saturated relatives, the Os—C and C—C distances are also in accord with the unsaturated nature of **4–Os**. Not surprisingly, the compound is also more stable than the diosmacyclobutanes and undergoes thermal CO substitution by PPh_3, as opposed to alkene loss from and fragmentation of the saturated four membered Os_2C_2 rings.[12] Interestingly, and perhaps as a result of the enhanced stability of the unsaturated dimetallacyclobutenes, the analogous diruthenacyclobutene, **4–Ru**, is also accessible from the photoreaction between $Ru_3(CO)_{12}$ and DMAD [eq. (6)].[20] The compounds **4–Os** and **4–Ru** are isomorphous and isostructural.

$$Ru_3(CO)_{12} + DMAD \xrightarrow[\text{pentane, RT}]{h\nu > 370\,\text{nm}}$$

$$Ru_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-DMAD})$$

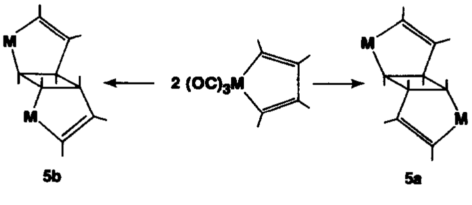
4–Ru

$$+ Ru_2(CO)_6(DMAD)_4 + C_6(CO_2CH_3)_6. \qquad (6)$$

5a–Ru, 5b–Ru

As with osmium, this reaction is accompanied by the formation of another product, **5–Ru**. Indeed, in this case the material is present under two isomeric forms, **5a–Ru** and **5b–Ru**. Spectroscopic work showed that the osmium compound corresponds to isomer **5a**.

The structures of the osmium compound, **5a–Os**, and the isomeric **5b–Ru** are shown in Fig. 4. The compounds are seen to arise from what can be considered "head-to-tail", **5a** and "head-to-head", **5b**, dimerization of the 16 electron metallacyclopentadiene, $M(CO)_3[C_4(CO_2CH_3)_4]$, [eq. (7)].



(7)

5b **5a**

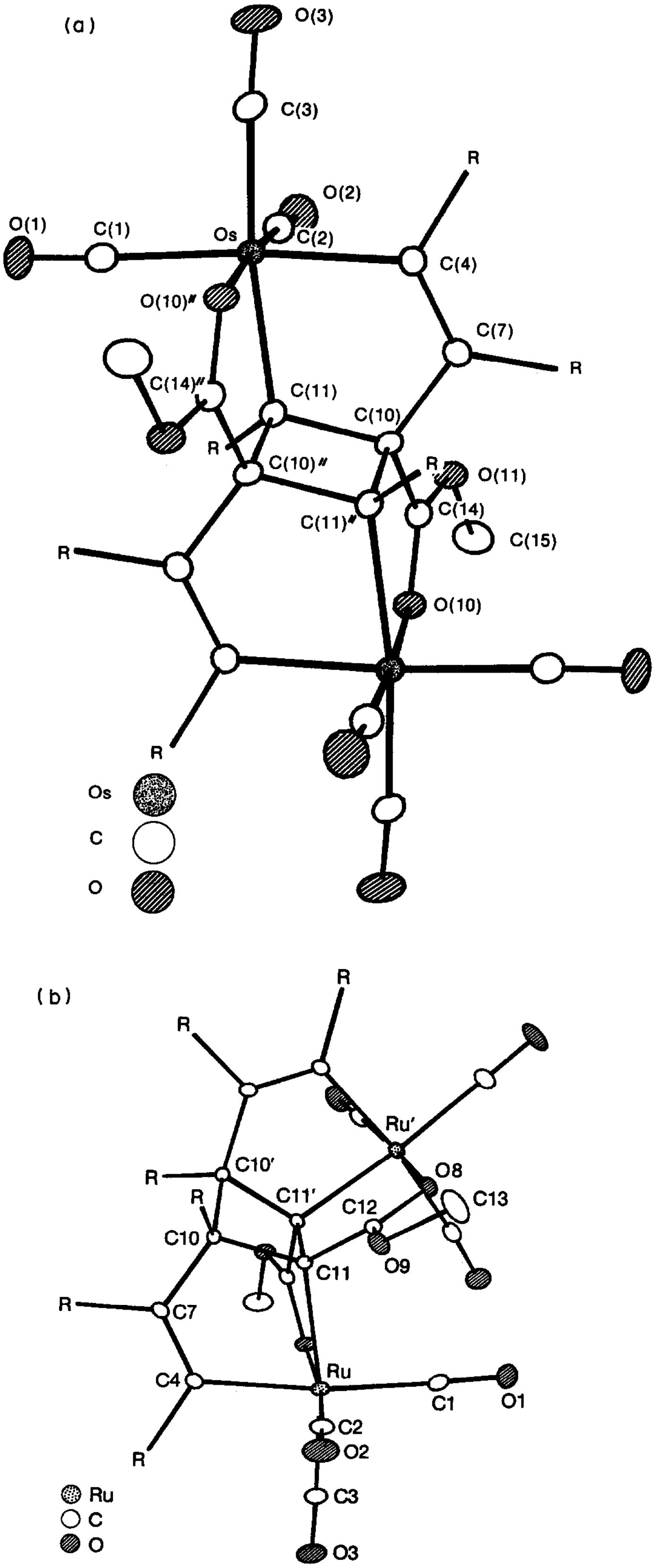


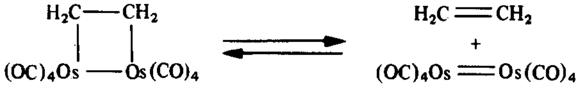
Fig. 4. Perspective views of (a) $Os_2(CO)_6(DMAD)_4$,[19] **5a–Os** and (b) $Ru_2(CO)_6(DMAD)_4$,[20] **5b–Ru**. Primed atoms are related by the centre of symmetry and the C_2 axis of symmetry, respectively. R represents the CO_2CH_3 group.

End-on coordination of a carboxylate oxygen donor completes the electronic demand of each metal. This is clearly evidenced by the lengthening of the C=O distance (~ 1.25 vs 1.19 Å for the unbound moieties) and the appearance of a low frequency C=O stretching frequency absorption around 1600 cm^{-1}. The coupling of the alkyne units is thus different from the usual sequential addition of one to four alkyne units to dimetallic centres.[3(a),(c)] It is noteworthy that from a thermal reaction Bruce *et al.*[21] identified two ruthenium containing compounds, $Ru_3(CO)_7(DMAD)_4$ and $Ru_2(CO)_6(DMAD)_2$, both different from the photoproducts described here.

The photoreaction of **1–Os** was also carried out with bis(trimethylsilyl)acetylene (BTMSA), hexafluorobut-2-yne (HFB), diphenylacetylene (DPA) and acetylene. Although the reaction with BTMSA led to the isolation of the first simple tetracarbonyl alkyne osmium compound,[22] $Os(CO)_4(\eta^2\text{-BTMSA})$ and paved the way for the preparation of the analogous ruthenium compound,[22] the other alkynes gave disappointing results. The reactions led to complicated and difficult to separate mixtures of products, many accessible from thermal reactions. Diosmacyclobutenes were seen with HFB and DPA, but isolated yields were exceedingly small.

ALKENE EXCHANGE IN $Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-}CH_2CHR)$ (R = CO_2CH_3, H)

The problems encountered already in the photoreaction of $Os_3(CO)_{12}$ with certain alkenes and even more extensively with alkynes, clearly indicated the necessity of an alternate synthetic route if we hoped to extend the number of known diosmacycles. Since, naively, we envisaged the formation of $Os_2(CO)_8(\mu\text{-}C_2H_4)$, **3a**, as arising from the interception of nascent $Os_2(CO)_8$ by ethylene, it seemed plausible that reversal of this process, [eq. (8)], could yield the reactive diosmium fragment which could then be scavenged by other unsaturated organic substrates giving other diosmacycles.



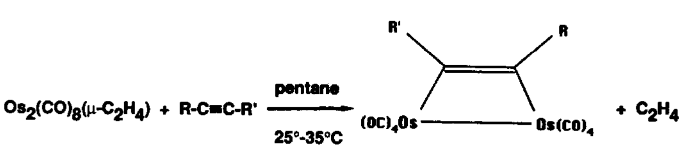
(8)

The attractive feature of such an approach was the ready availability of **3a** in moderate yields (see above).

Although from the isolobal relation between **3a** and cyclobutane,[23] fragmentation of **3a**, as shown in eq. (8), is a symmetry forbidden process,† Trinquier and Hoffman[24] have shown that the activation barrier to such a dinuclear reductive elimination process is significantly lowered when the leaving groups are tied together, as in **3a**. Indeed, anticipating some of the results, elimination of ethylene from **3a** is facile and in solution occurs already at around 30°C, albeit slowly. More surprisingly, some recent very elegant experiments by Norton[25] have established that the elimination is stereospecific and as such, contrary to the symmetry rules, most probably proceeds via a concerted process.

Exchange reactions with alkynes

The initial experiment between $Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-}CH_2CHCO_2CH_3)$ **3b**, and DMAD was encouraging. Although a temperature of 80°C was required to give convenient conversion rates, a yield of 47% of the diosmacyclobutene, **4–Os**, was obtained.[19]‡ However, the high temperature necessary for exchange was deleterious with other alkynes and consequently contemporary exchange reactions involve **3a** [eq. (9)].[27]



(9)

R	R′	Yield (%)
CO_2Me	CO_2Me	50 (68§)
Ph	Ph	20 (32§)
H	COMe	70
H	CO_2Me	70
CF_3	CF_3	5–20

It should be noted that the thermal exchange reaction can also be used to prepare saturated diosmacyclobutanes which are more robust than **3a** and/or **3b**. Heating **3b** with excess maleic anhydride

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† The forward reaction, or further reaction of $Os_2(CO)_8$ with double or triple bonds is also a symmetry forbidden thermal process. It is the organometallic analogue of the organic $[2\pi_s+2\pi_s]$ cycloaddition reaction.

‡ For the use of DMAD as a trapping agent in a related dimetalla-Diels–Alder reaction ($[4\pi_s+2\pi_s]$ cycloaddition) involving the six-membered benzodicobaltacyclohexane ring, $Cp_2Co_2(\mu\text{-}CO)_2(\mu\text{-}o\text{-xylylene})$, see Hersch and Bergman.[26]

§ The yields in parentheses refer to photochemical exchange reaction.

gave $Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-CHCHC(O)OC(O)})$ in 54% isolated yield. This material, as indicated before, is not accessible via photolysis.

The improved yield of **4–Os** and the isolation of the DPA and HFB bridged compounds in quantities sufficient for full characterization, clearly indicate the superiority of the thermal exchange method over the photolysis of $Os_3(CO)_{12}$ and alkynes. Unfortunately the procedure is not universal in its application. Already the reaction with DPA is accompanied by the formation of other products including $Os_3(CO)_{12}$, a ubiquitous by-product in many reactions. Similar problems have been encountered with acetylene and HFB. Indeed the parent diosmacyclobutene, $Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-HCCH})$, has so far defied isolation. Also puzzling is the reaction with HFB which also gave mixtures of products. That the problem is not associated with some peculiar property of the product diosmacyclobutene, $Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-HFB})$, is evidenced by an interesting and unusual alternate synthesis which can be extended to the RuRu and mixed RuOs compounds as well. In a very interesting development we have discovered that the 18 electron $M(CO)_4(\eta^2\text{-HFB})$ (M = Ru, Os) complexes react further with the respective pentacarbonyls to produce dimetallacyclobutenes in good yields [eq. (10)].[28] No solid state structural work is yet available, but the proper formulation of the compounds was ascertained by spectroscopic techniques, the ^{13}C NMR spectra being especially valuable.

$$M(CO)_4(\eta^2\text{-HFB}) + M'(CO)_5 \xrightarrow[\text{alkane}]{\Delta} MM'(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-HFB}) \quad (10)$$

M	M′	MM′	Δ	Yield
M = Ru	M′ = Ru	MM′ = RuRu	25°C	73%
Os	Os	OsOs	60°C	66%
Ru	Os	RuOs	25°C	77%

The limiting spectra are shown in Fig. 5. The number and intensity distribution of the peaks are clearly consistent with the proposed structures. The spectra provide a nice illustration of the predictable upfield shifts of the carbonyl signals as the metal triad is descended.[29] With the exception of the OsOs compound, which is rigid at room temperature, the molecules are fluxional. The intermetallic carbonyl exchange proceeds most plausibly via the "merry-go-round" process[30] which exchanges the environments of carbonyl groups lying in a plane, leaving one, the unique CO *trans* to the parallel alkyne bridge, invariant. The activation energy for interchange follows RuRu (11.0 kcal mol^{-1}) < RuOs (14.4 kcal mol^{-1}) < OsOs (static at room temperature).

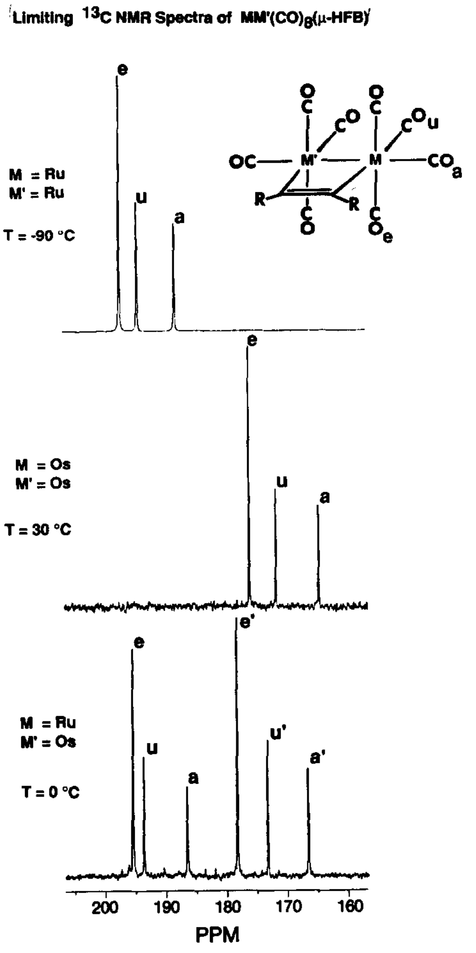
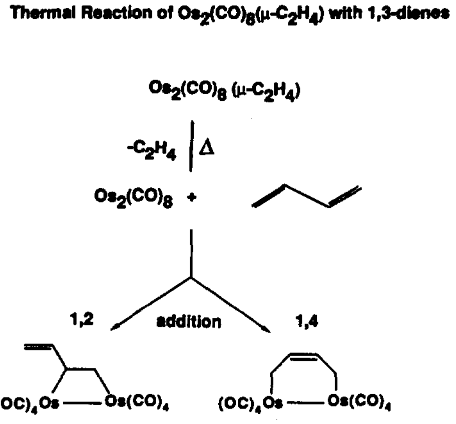


Fig. 5. Limiting ^{13}C NMR spectra of $MM'(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-HFB})$ molecules.[28]

Exchange reactions with dienes

The thermal reaction between **3a** and 1,3-dienes was initiated with the hope of producing diosmacycles with different ring sizes. Indeed as shown in eq. (11), the reaction in principle can proceed via 1,2- and/or 1,4-addition, yielding four-and six-membered diosmacycles, respectively. Although the 1,2-type addition with **3a** is now firmly established, in view of the precedented dimetalla-Diels–Alder type reaction,[26] the 1,4-addition can not be dismissed lightly.

The reaction between **3a** and diethylmuconate (MUCO) gave $Os_2(CO)_8(MUCO)$ in good yield.[31] The complex ^{13}C NMR spectrum, Fig. 6, clearly implies the formation of a 1,2-adduct. Trace amounts of an isomeric product were also isolated from this reaction which may be the symmetric 1,4-



(11)

adduct. Efforts are underway to identify appropriate reaction conditions to favour the Diels–Alder path. Similar 1,2-addition occurred with two heterodienes,[31] Table 1. The reaction with the diazadiene ligand gave the aza-diosmacyclobutane $Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-Gpi})$, in 35% isolated yield (^{13}C NMR spectrum, Fig. 7) and represents a new type of bonding of this ligand system on dimetallic centres.[32] The reaction with *trans*-benzalacetone gave only a single, *trans* adduct and as such represents an interesting example of regio- and stereospecific 1,2-addition. Thus, although our initial goal of preparing diosmacycles with a larger ring size has been temporarily aborted, the prospect of obtaining diosmacycles with different heteroatoms and functional groups for further derivatization is nevertheless encouraging.

It would be less than candid to close this section by giving the impression that the thermal exchange reactions are not without difficulties. Problems were encountered especially with "unactivated" dienes. In an effort to promote the 1,4-addition, the reactions with cyclopentadiene (CpH), 2,3-dimethyl-1,3-butadiene (DMBU) and 2-trimethylsiloxy-1,3-butadiene (TSBU) were carried out. No reaction was observed with CpH. The reaction with DMBU gave mostly $Os_3(CO)_{12}$ and a small amount of $Os(CO)_3(\eta^4\text{-DMBU})$, whereas with TSBU a very slow 1,2-addition to the unsubstituted double bond occurred.[31] Believing that at least part of the difficulties are associated with the thermal fragility of the newly formed diosmacycles, current efforts are centred on the photochemically induced ethylene exchange from **3a**.

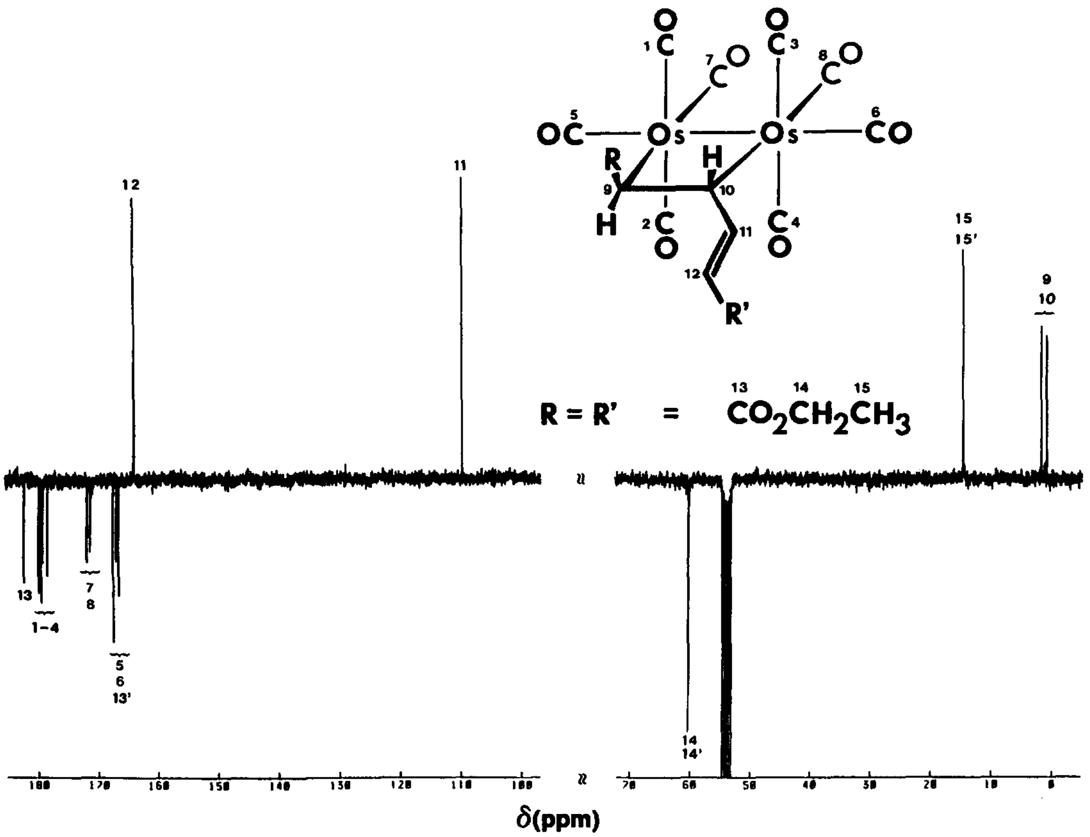
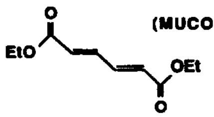
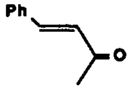
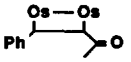


Fig. 6. APT ^{13}C NMR spectrum of $Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-diethylmuconate})$.[31]

Table 1. Thermal reaction of $Os_2(CO)_8(\mu\text{-}C_2H_4)$ with "dienes"

Diene		Product(s)	Addition
(1) 	(MUCO)	$Os_2(CO)_8(\mu\text{-MUCO})$	1,2 (C,C)
(2) 	(Gpl)	$Os_2(CO)_8(\mu\text{-Gpl})$	1,2 (C,N)
(3) 	(BEAC)	$Os_2(CO)_8(\mu\text{-BEAC})$ 	1,2 (C,C)

REACTIVITY OF THE DIOSMACYCLOBUTANES: HYDRIDE ABSTRACTION FROM $Os_2(CO)_8(\mu\text{-}C_2H_4)$

An important aspect of the chemistry of dimetallacyclic compounds is the thesis that such molecules may serve as useful models for the surface transformations of unsaturated organic substrates. As a first test of hydrogen mobility, hydride abstraction from $Os_2(CO)_8(\mu\text{-}C_2H_4)$, **3a**, was investigated. The reaction of **3a** with Ph_3CBF_4 proceeded readily and gave the $\mu\text{-}\eta^1,\eta^2$-vinyl complex **6** in excellent yield [eq. (12)].[33]

$$\mathbf{3a} + Ph_3CBF_4 \xrightarrow[RT]{CH_2Cl_2} [Os_2(CO)_8(\mu\text{-}\eta^1,\eta^2\text{-}C_2H_3)]BF_4. \quad (12)$$

6 (92%)

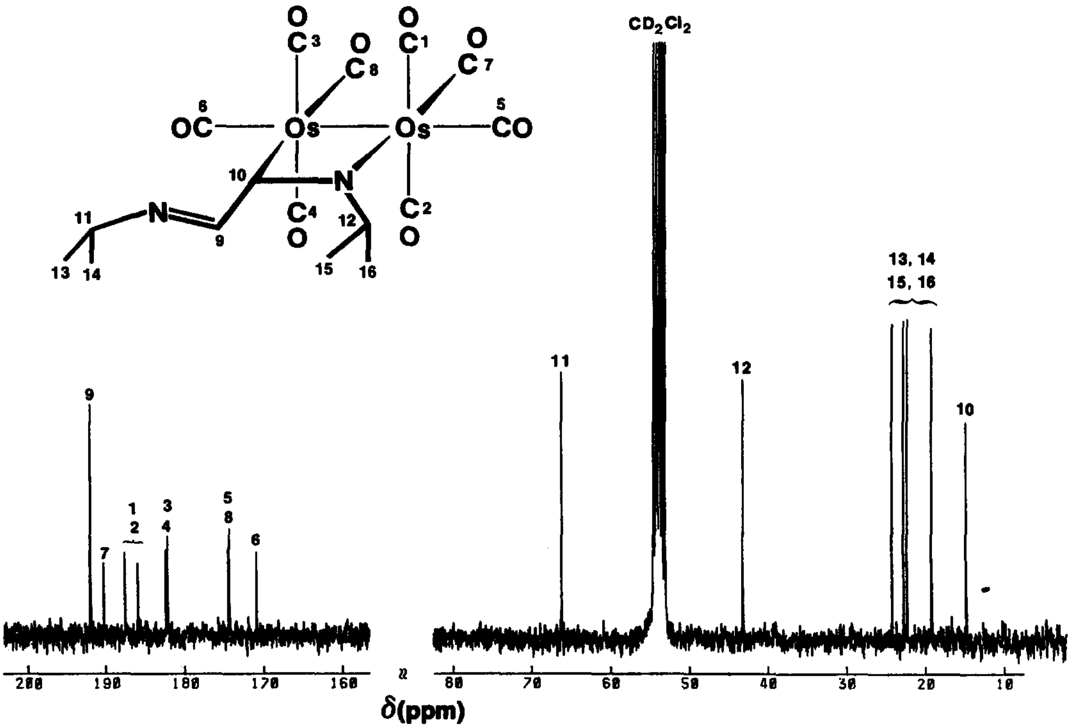


Fig. 7. ^{13}C NMR spectrum of $Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-}C\text{-glyoxalbis(isopropylimine)})$.[31]

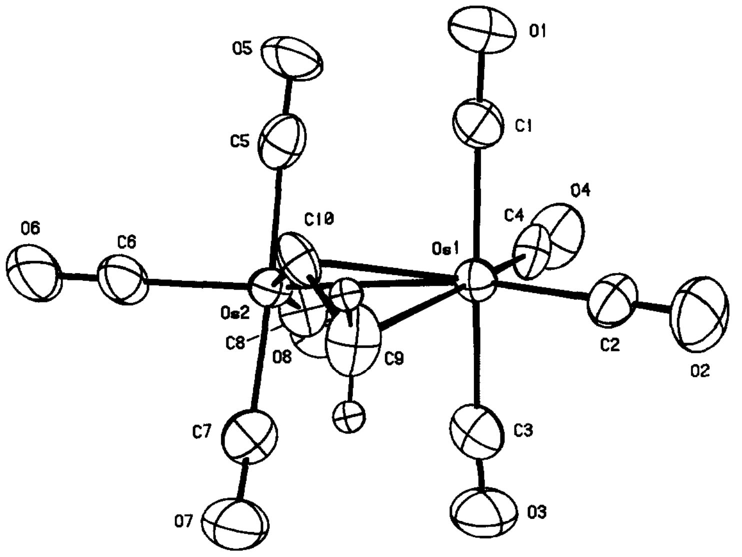


Fig. 8. Molecular structure of $Os_2(CO)_8(\mu\text{-}\eta^1,\eta^2\text{-}CHCH_2)^+$, **6**.[33] Relevant bond distances (Å): Os(1)—Os(2) = 2.8569(5), Os(2)—C(10) = 2.061(9), Os(1)—C(10) = 2.30(1), Os(1)—C(9) = 2.34(1), C(9)—C(10) = 1.41(2).

The structure of **6** is shown in Fig. 8. A characteristic feature of the μ-CH moiety in related vinyl bridged cationic species is the μ-carbenoid nature of this group, which is reflected in the low field NMR position of the μ-CH carbon and hydrogen atoms[34] and the nearly symmetrical metal–carbon distances.[35] This type of behaviour is manifested in the present complex as well, although perhaps to a more limited extent. Indeed the μ-C$\underline{H}$ ($\delta = 8.56$ ppm) and μ-$\underline{C}$H ($\delta = 134.9$ ppm) resonance positions are at higher, whereas the $\underline{C}H_2$ signal ($\delta = 64.8$ ppm) is at lower field than expected. Also, the Os(2)—C(10) interaction, 2.06(1) Å is significantly shorter than the Os(1)—C(10), 2.30(1) Å distance, indicative of a greater contribution from σ,π-vinyl type bonding in this compound.† Interestingly the bonding changes appear to have a noticeable effect on both physical and chemical properties of **6**. Thus, contrary to other μ-η^1,η^2-vinyl complexes which are fluxional in solution,[34,37] **6** remains rigid up to 90°C Also, as opposed to the normal behaviour of the related compounds which undergo hydride addition to the β-carbon of the μ-vinyl group and generate μ-carbene complexes,[34] hydride attack on **6** initially occurs at the α-carbon and regenerates the original 1,2-diosmacyclobutane, **3a**.

Attempts to deprotonate **6** proved unsuccessful. Even hindered bases like KO^{t}Bu and DBU acted as nucleophiles and $NaN(SiMe_3)_2$ led to decomposition. The reaction with PMe_3 gave a single product. The ^{13}C NMR features at -21.2 ppm (d, $J_{P\text{—}C} = 25.9$ Hz, $\underline{C}HPMe_3$) and -28.6 ppm (d, $J_{P\text{—}C} = 8.3$ Hz, $\underline{C}H_2$), clearly show the formation of a substituted 1,2-diosmacyclobutane [eq. (13)].

$$\mathbf{6} + PMe_3 \xrightarrow[RT]{acetone}$$

$$[Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-}CH_2CHPMe_3]BF_4. \quad (13)$$

CONCLUSION

A serendipitous discovery led to the synthesis of a modest number of saturated 1,2-diosmacyclobutanes. The hope that the simple photochemical route could be extended and would allow the preparation of a wide range of diosmacyclic compounds proved short lived. This resulted in a search for a more rational synthesis of such compounds. Although not without problems, the thermally and/or photochemically induced ethylene exchange reaction from $Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-}C_2H_4)$ has already proved useful in this regard. The scope of this reaction and the chemistry of the derived diosmacycles is of continuing interest to us.‡

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† A more pronounced distortion of the bridging vinyl group in $W_2Cl_3(NMe_2)_2(CHCH_2)(PMe_2Ph)_2$, led Chisholm[36] to postulate a tendency towards "terminal" metal–carbene type interaction of the CH moiety in this compound.

‡ The utility of $Os_2(CO)_9$ as a source of $Os_2(CO)_8$ for reactions with unsaturated substrates is being explored by J. R. Norton and his co-workers, personal communication.

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REFERENCES

1. Two recent reviews deal with the chemistry of hydrocarbon-bridged dinuclear transition metal complexes. (a) C. P. Casey and J. D. Audett, *Chem. Rev.* 1986, **86**, 339; (b) J. R. Moss and L. G. Scott, *Coord. Chem. Rev.* 1984, **60**, 171.
2. W. A. Hermann, *J. Organomet. Chem.* 1983, **250**, 319; W. A. Herman *Adv. Organomet. Chem.* 1982, **20**, 159.
3. (a) M. D. Curtis, *Polyhedron* 1987, **6**, 759; (b) M. Chisholm, B. K. Conroy, B. W. Eichhorn, K. Falting, D. M. Hoffman, J. C. Huffman and N. S. Marchant, *Polyhedron* 1987, **6**, 783; (c) S. A. R. Knox, *Pure Appl. Chem.* 1984, **56**, 81; (d) R. S. Dickson, G. D. Fallon, S. M. Jenkins and R. J. Nesbit, *Organometallics* 1987, **6**, 1240.
4. For a delightful account of the origin of the word "serendipity" and its place in science see P. Laszlo, *Nou. J. Chimie* 1983, **7**, 675.
5. F.-W. Grevels, J. G. A. Reuvers and J. Takats, *J. Am. Chem. Soc.* 1981, **103**, 4069.
6. B. F. G. Johnson, J. Lewis and M. V. Twigg, *J. Chem. Soc., Dalton Trans* 1975, 1876.
7. D. R. Taylor, M. Altobelli and H. B. Gray, *J. Am. Chem. Soc.* 1980, **102**, 3022.
8. J. G. Bensten and M. S. Wrighton, *J. Am. Chem. Soc.* 1987, **109**, 4518.
9. M. R. Burke, J. Takats, F.-W. Grevels and J. G. A. Reuvers, *J. Am. Chem. Soc.* 1983, **105**, 4092.
10. K. M. Motyl, J. R. Norton, C. K. Schauer and O. P. Anderson, *J. Am. Chem. Soc.* 1982, **104**, 7325.
11. F.-W. Grevels, J. R. Norton, J. Takats *et al.*, *Inorg. Synth.*, to be submitted.
12. M. R. Burke, Ph.D. thesis, University of Alberta, Edmonton (1987).
13. A. J. Poë amd C. V. Sekhar, *J. Am. Chem. Soc.* 1986, **108**, 3673.
14. Ph. Vioget, M. Bonivento, R. Roulet and P. Vogel, *Helv. Chim. Acta* 1984, **67**, 1630.
15. J. R. Norton, personal communication of unpublished results.
16. (a) J. Malito, S. Markiewicz and A. J. Poë, *Inorg. Chem.* 1982, **21**, 4335; (b) M. F. Desrosiers, D. A. Wink, R. Trautman, A. E. Friedman and P. C. Ford, *J. Am. Chem. Soc.* 1986, **108**, 1917; (c) J. G. Bensten and M. S. Wrighton, *J. Am. Chem. Soc.* 1987, **109**, 4530.
17. P. R. Raithby and M. J. Rosales, *Adv. Inorg. Chem. Radiochem.* 1985, **29**, 169.
18. D. M. Hoffman, R. Hoffmann and C. A. Friesel, *J. Am. Chem. Soc.* 1982, **104**, 3858.
19. M. R. Burke and J. Takats, *J. Organomet. Chem.* 1986, **302**, C25.
20. R. G. Ball, M. R. Gagné and J. Takats, to be submitted.
21. M. I. Bruce, J. G. Matisons, B. W. Skelton and A. H. White, *J. Organomet. Chem.* 1983, **251**, 249.
22. R. G. Ball, M. R. Burke and J. Takats, *Organometallics* 1987, **6**, 1918.
23. (a) R. Hoffmann, *Angew. Chem. Int. Ed. Engl.* 1982, **21**, 711; (b) T. A. Albright, J. K. Burdett and M.-H. Whangbo, *Orbital Interactions in Chemistry*. Wiley-Interscience, New York (1985).
24. G. Trinquier and R. Hoffmann, *Organometallics* 1984, **3**, 370.
25. R. T. Hembre, C. P. Scott and J. R. Norton, *J. Am. Chem. Soc.* 1987, **109**, 3468.
26. W. H. Hersch and R. G. Bergman, *J. Am. Chem. Soc.* 1983, **105**, 5846.
27. M. R. Burke, F. Seils and J. Takats, to be submitted.
28. M. R. Gagné and J. Takats, *Organometallics*, in press.
29. B. E. Mann and B. F. Taylor, *^{13}C NMR Data for Organometallic Compounds*. Academic Press, New York (1981).
30. E. Bond and E. Muetterties, *Chem. Rev.* 1978, **28**, 639.
31. F. Seils and J. Takats, unpublished results.
32. G. van Koten and K. Vrieze, *Adv. Organomet. Chem.* 1982, **21**, 151.
33. F.-W. Grevels, W. A. Kiel and J. Takats, unpublished results.
34. (a) A. F. Dyke, S. A. R. Knox, M. J. Morris and P. J. Naish, *J. Chem. Soc., Dalton Trans.* 1983, 1417; (b) C. P. Casey, S. R. Marder and B. R. Adams, *J. Am. Chem. Soc.* 1985, **107**, 7700.
35. A. G. Orpen, *J. Chem. Soc., Dalton Trans.* 1983, 1427 and refs therein.
36. K. J. Ahmed, M. H. Chisholm, K. Folting and J. C. H. Hoffmann, *J. Am. Chem. Soc.* 1986, **108**, 989.
37. J. R. Shapley, S. I. Richter, M. Tachikawa and J. B. Keister, *J. Organomet. Chem.* 1975, **95**, C43.

Note added in proof. The parent diosmacyclobutene, $Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-}C_2H_2)$, has since been isolated and characterized. Seen in the exchange reactions between **3a** and acetylene, the cleanest preparation so far discovered involves self condensation of $Os(CO)_4(\eta^2\text{-}C_2H_2)$; G.-Y. Kiel, F. Seils and J. Takats, unpublished results.