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Oxo-bridged metal carbene complexes. Synthesis, structure and reactivities of {[Os(Por)(CPh$_2$)]$_2$O} (Por = porphyrinato dianion)†

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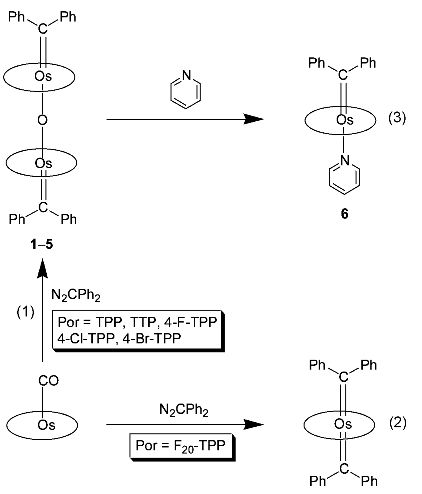
Dinuclear μ-oxo osmium porphyrins containing terminal Os=CPh$_2$ bonds with a linear C=Os–O–Os=C moiety were prepared, which are reactive toward pyridine to form [Os(Por)(CPh$_2$)(py)] and are active catalysts for inter- and intra-molecular cyclopropanation of alkenes and for carbene insertion into saturated C–H bonds.

The widely-believed involvement of metal carbene intermediates in several biological processes[1,2] and synthetic catalytic C–C bond formation reactions[3] has stimulated much interest in metal carbene complexes. Numerous mononuclear metal carbene complexes have been isolated and structurally characterised;[1–6] however, polynuclear metal complexes bearing terminal carbene groups are sparse. Herein we report a series of air-stable dinuclear oxo-bridged osmium porphyrin carbene complexes, {[Os(Por)(CPh$_2$)]$_2$O} (Por = TPP: **1**, TTP: **2**, 4-F-TPP: **3**, 4-Cl-TPP: **4**, 4-Br-TPP: **5**),‡ which, to the best of our knowledge, represents the first μ-oxo dimers of metalloporphyrins containing terminal carbene ligands.

Complexes **1–5** were prepared in 58–80% yields from reactions of [Os(Por)(CO)] with excess diphenyldiazomethane at room temperature in benzene or dichloromethane solutions exposed to air (reaction 1 in Scheme 1). We note that the same reaction for Por = F$_{20}$-TPP‡ gave bis(carbene) osmium complex [Os(F$_{20}$-TPP)(CPh$_2$)$_2$] in good yield (reaction 2 in Scheme 1).[7] Evidently, the highly electron-deficient nature of F$_{20}$-TPP is essential for stabilising the bis(carbene) species.



Scheme 1

Unlike the cyclopropanation-active bis(carbene) complex [Os(F$_{20}$-TPP)(CPh$_2$)$_2$],[7] complexes **1–5** underwent no carbene group transfer reactions with styrene to give 1,1,2-triphenylcyclopropane even at 80 °C for 30 h. Interestingly, treatment of **1–5** with pyridine can convert the μ-oxo dimers into mononuclear osmium porphyrin carbene complexes. For example, treatment of **2** with excess pyridine in refluxing benzene for 20 h afforded [Os(TTP)(CPh$_2$)(py)] (**6**) in about 40% yield (reaction 3 in Scheme 1).

The NMR, UV/Vis, IR, and mass spectral data of **1–6** are compiled in the ESI.† These osmium porphyrin carbene complexes exhibit ^{13}C NMR signal of Os=*C*Ph$_2$ in the range of δ = 266–279. Complexes **1–5** show UV/Vis spectra and ^{1}H NMR signals for the porphyrin ligands that resemble those of previously reported diamagnetic μ-oxo osmium porphyrins {[Os^{IV}(Por)X]$_2$O} (X = RO$^-$, RS$^-$).[8,9] The key spectral features of **6** are similar to those of mononuclear carbene complex [Os(F$_{20}$-TPP)(CPh$_2$)],[7] both of which give considerably upfield-shifted porphyrin pyrrole proton signals and downfield-shifted CPh$_2$ phenyl signals in the ^{1}H NMR spectra (compared with **1–5**). Since the ^{1}H NMR signals of **1–5** appear at normal fields and their chemical shifts are insignificantly dependent on temperature (*e.g.* $\Delta\delta \leq 0.10$ ppm for **1** in the range of 20 to −60 °C), these μ-oxo bridged carbene complexes should be diamagnetic. A comparison of the IR "oxidation state marker" band of **1** (1016 cm^{-1}) with those of [Os^{VI}(TPP)O$_2$] (1021 cm^{-1}), [Os^{VI}(TPP)(NBu^t)$_2$] (1017 cm^{-1}) and [Os^{IV}(TPP)(OR)$_2$] (R = Me, Et; 1014 cm^{-1})[10] suggests an Os(V) formulation for **1–5**. Therefore the Os=CPh$_2$ moieties in **1–5** should adopt the Schrock type formulation with a polarised Os=CPh$_2$ bond.

We have determined the structures of **2** and **6** by X-ray crystallography (Figs. 1 and 2).§ Complex **2** shows a linear axial

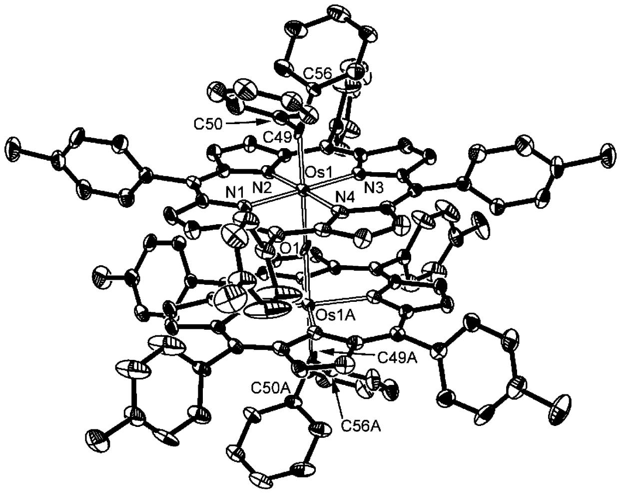


Fig. 1 ORTEP drawing of **2**. Selected bond lengths (Å) and angles (°): Os1–O1 1.910(1), Os1–C49 1.910(4); Os1–O1–Os1A 179.4(2), C49–Os1–O1 179.0(1), C50–C49–C56 110.7(3).

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† Electronic supplementary information (ESI) available: detailed procedures for the preparation of **1–6** and for the cyclopropanation and C–H insertion reactions catalysed by **2**; NMR, IR, UV/Vis, mass spectral data and elemental analyses for **1–6**; Tables of yields and conversions for cyclopropanations catalysed by **2**. See http://www.rsc.org/suppdata/cc/b3/b300441d/

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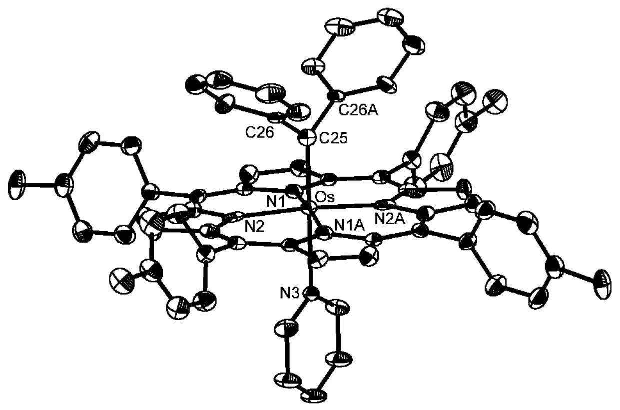


Fig. 2 ORTEP drawing of **6**. Selected bond lengths (Å) and angles (°): Os–C25 1.903(7), Os–N3 2.318(5); C26–C25–C26A 112.4(6), C25–Os–N3 180.000(2).

C=Os–O–Os=C moiety with an Os–O distance of 1.910(1) Å and an Os–O–Os angle of 179.4(2)°. Such dimensions are comparable with those of {[Os^{IV}(OEP)(OMe)]$_2$O} [1.807(3) Å and 177(2)°][11] and {[Os^{IV}(OEP)(NO)]$_2$O} [2.0945(5) Å and 180.0°].[12] The two axial Ph–C–Ph carbene planes are nearly coplanar, making a small dihedral angle of 4.5° [the sum of the Os–C49–C50, C50–C49–C56, and Os–C49–C56 angles is 360.0(3)°]. The two porphyrin rings are distorted 27.1° from the eclipsed conformation, which is probably caused by steric interactions. Complex **6**, the sole structurally characterised metalloporphyrin carbene complex with a *trans* pyridine ligand, exhibits a structure similar to those of [Os(F_{20}–TPP)(CPh_2)(MeOH)][7] and [Os(TTP)(C(*p*-$C_6H_4CH_3$)$_2$)(THF)].[13] The Os=CPh_2 bond lengths of **2** [1.910(4) Å] and **6** [1.903(7) Å] are similar, both are slightly longer than the Os=C(carbene) bond lengths found in [Os(F_{20}-TPP)(CPh_2)(MeOH)] [1.870(2) Å][7] and [Os(TTP)(C(*p*-$C_6H_4CH_3$)$_2$)(THF)] [1.865(5) Å].[13] The Os atoms in **2** and **6** are basically situated in the corresponding porphyrin ring planes, with a displacement (from the N_4 least-squares plane) of 0.0289 Å (toward the μ-oxo ligand) in **2** and 0.083 Å (toward the carbene ligand) in **6**.

On the basis of the linear C=Os–O–Os=C configuration and the co-planarity of the two carbene planes in the structure of **2**, we propose that there is delocalised C–Os–O–Os–C and Os–O–Os π-bonding (see Fig. 3) in **1–5**. These π-bonding interactions result in coupling of the unpaired electrons of the two oxo-bridged Os atoms [a clear distinction between Os(V) and Os(III) formulation remains difficult, though the oxidation state marker band prefers the former formulation], rendering the complexes diamagnetic.

Although none of the previously known μ-oxo osmium porphyrins are reported to exhibit catalytic activity toward organic transformations, complexes **1–5** are active catalysts for intermolecular cyclopropanation of styrenes with EDA‡ (see Table S1 in ESI†) and for intramolecular cyclopropanation of allylic diazoacetates (see Table S2 in ESI†). When a CH_2Cl_2 solution of EDA was added to a solution of **2** (0.1 mol% relative to EDA) and excess styrene in CH_2Cl_2 over 5 h at room temperature, the cyclopropanation product was formed in 99% yield with 100% EDA conversion. The diastereoselectivity (*trans* : *cis* = 9.4 : 1) was similar to, whereas the catalytic turnover number (990) was higher than, that observed with catalyst [Os(TTP)]$_2$ (*trans* : *cis* = 10.2 : 1, turnover = 395).[14] When a CH_2Cl_2 solution of *cis*-pent-2-enyl diazoacetate was added dropwise to a solution of **2** in CH_2Cl_2 (0.05 mol%) at 40 °C over 10 h, the intramolecular cyclopropanation product was formed in 78% yield with 95% conversion.

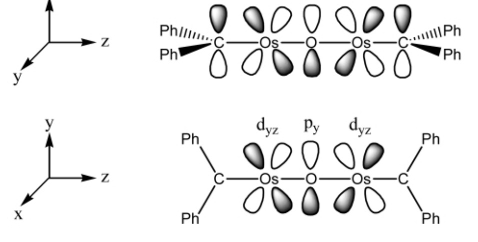
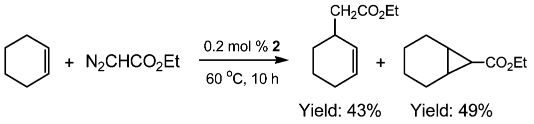


Fig. 3 Proposed π-bonding interactions in **1–5**.

We previously reported stoichiometric C–H insertion reactions of osmium[7] and iron[15] carbene complexes with hydrocarbons. Interestingly, complex **2** can catalyse the reaction of cyclohexene with EDA to give an allylic C–H insertion product in 43% yield (reaction 4).



(4)

To our knowledge, this is the first intermolecular carbene insertion into C–H bonds catalysed by a metalloporphyrin.

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Notes and references

‡ Abbreviations: H_2TPP: 5,10,15,20-tetraphenylporphyrin; H_2TTP: 5,10,15,20-tetrakis(*p*-tolyl)porphyrin; H_2(4-F-TPP): 5,10,15,20-tetrakis-(*p*-fluorophenyl)porphyrin; H_2(4-Cl-TPP): 5,10,15,20-tetrakis(*p*-chlorophenyl)porphyrin; H_2(4-Br-TPP): 5,10,15,20-tetrakis(*p*-bromophenyl)porphyrin; H_2(F_{20}-TPP): 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin; EDA: ethyl diazoacetate.

§ *Crystal data* for **2**: $C_{122}H_{92}N_8OOs_2$, M = 2066.44, monoclinic, a = 24.106(3), b = 16.824(2), c = 28.651(4) Å, β = 107.618(3)°, V = 11075(2) Å^3, T = 294 K, space group $C2/c$, Z = 4, μ(Mo-Kα) = 2.342 mm^{-1}, 37230 reflections measured, 12657 unique (R_{int} = 0.090), final R indices [$I > 2\sigma(I)$] $R1$ = 0.061, $wR2$ = 0.126. CCDC reference number 201472.

For **6**: $C_{66}H_{51}N_5Os$, M = 1104.32, monoclinic, a = 14.670(5), b = 11.581(4), c = 16.707(5) Å, β = 105.290(7)°, V = 2738(2) Å^3, T = 294 K, space group $P2/n$, Z = 2, μ(Mo-Kα) = 2.373 mm^{-1}, 17727 reflections measured, 6277 unique (R_{int} = 0.12), final R indices [$I > 2\sigma(I)$] $R1$ = 0.060, $wR2$ = 0.089. CCDC reference number 201471. See http://www.rsc.org/suppdata/cc/b3/b300441d/ for crystallographic data in CIF or other electronic format.

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