Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

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

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Experimental Section

Dichloromethane was distilled from calcium hydride before use. Diphenyldiazomethane,[1] allylic diazoacetates[2] and all porphyrinato osmium carbonyl complexes[3] were prepared according to the literature methods. Various alkenes purchased from Aldrich were purified by passing through aluminum oxide. UV-visible spectra were recorded on a HP 8453 Diode Array spectrophotometer. Infra-red spectra were obtained on a BIO-RAD FTS 165 spectrometer. Mass spectra were recorded on a Finnigan MAT 95 mass spectrometer. GC-MS measurements were performed on a HP G1800C GCD Series II spectrometer with an Ultra 2 cross-linked 5% phenyl-methyl silicone column (25 m × 0.2 mm × 0.33 μm). ^{1}H NMR and ^{13}C NMR spectra were obtained using Bruker DPX-300 FT-NMR spectrometer; the chemical sifts (δ, ppm) are relative to tetramethylsilane (*J* values are given in Hz). Elemental analyses were performed by the Institute of Chemistry, the Chinese Academy of Sciences.

General procedure for preparation of {[Os(Por)(CPh$_2$)]$_2$O}: To a solution of [Os(Por)(CO)] (0.05 mmol, 10 ml) in benzene was added a solution of N_2CPh_2 (38.8 mg, 0.20 mmol) in the same solvent (10 ml) using syringe pump over 10 h at room temperature. The mixture was evaporated under reduced pressure. The desired product was purified by chromatography on alumina column using dichloromethane/hexane (1:2 v/v) as eluent.

{[Os(TPP)(CPh$_2$)]$_2$O} (1): Yield: 80%; ^{1}H NMR ($CDCl_3$): δ 8.71 (d, 8H, 7.43), 8.12 (s, 16H, H$_\beta$), 7.81 (t, 8H, 7.57), 7.72 (t, 8H, 7.68), 7.49 (t, 8H, 7.48), 7.05 (d, 8H, 7.42), 5.71 (t, 4H, 7.18), 5.45 (t, 8H, 7.69), 1.21 (d, 8H, 7.66); ^{13}C NMR ($CDCl_3$): δ 268.84 (Os=C); UV/vis (CH_2Cl_2): λ_{max}/nm (log ε) 408 (5.10), 529 (4.20), 607 (3.95), 735 (3.95); IR (KBr): 1016 cm^{-1} (oxidation state marker band); Anal. Calcd for $C_{114}H_{76}N_8OOs_2$: C 70.06, H 3.92, N 5.73; Found: C 69.64, H 4.14, N 5.26; FAB MS: *m*/*z* 1955 [M + H]$^+$.

{[Os(TTP)(CPh$_2$)]$_2$O} (2): Yield: 74%; ^{1}H NMR ($CDCl_3$): δ 8.71 (d, 8H, 7.55), 8.08 (s, 16H, H$_\beta$), 7.61 (d, 8H, 7.57), 7.29 (d, 8H, 7.52), 6.95 (d, 8H, 7.52), 5.64 (t, 4H, 7.20), 5.41 (t, 8H, 7.57), 2.72 (s, 24H), 1.19 (d, 8H, 7.46); ^{13}C NMR ($CDCl_3$): δ 266.20 (Os=C); UV/vis (CH_2Cl_2): λ_{max}/nm (log ε) 413 (5.12), 532 (4.22), 613 (3.96), 734 (3.97); IR (KBr): 1016 cm^{-1} (oxidation state marker band); Anal. Calcd for $C_{122}H_{92}N_8OOs_2 \cdot C_6H_{14}$: C 71.41, H 4.96, N 5.20; Found: C 71.80, H 4.68, N 4.75; FAB MS: *m*/*z* 2067 [M + H]$^+$. The crystals suitable for X-ray structure determination were obtained by slow evaporation of a solution of **2** in dichloromethane-hexane at room temperature.

{[Os(4-F-TPP)(CPh$_2$)]$_2$O} (3): Yield: 80%; ^{1}H NMR ($CDCl_3$): δ 8.60–8.56 (m, 8H), 8.06 (s, 16H, H$_\beta$), 7.56–7.51 (m, 8H), 7.24–7.19 (m, 8H), 7.00–6.96 (m, 8H), 5.69 (t, 4H, 7.23), 5.44 (t, 8H, 7.66), 1.15 (d, 8H, 7.64); ^{13}C NMR ($CDCl_3$): δ 269.28 (Os=C); UV/vis (CH_2Cl_2): λ_{max}/nm (log ε) 409 (5.12), 530 (4.24), 605 (sh, 3.96), 734 (3.98); IR (KBr): 1015 cm^{-1} (oxidation state marker band); Anal. Calcd for $C_{114}H_{68}F_8N_8OOs_2 \cdot C_6H_{14}$: C 65.98, H 3.78, N 5.13; Found: C 66.24, H 3.84, N 4.88; FAB MS: *m*/*z* 2100 [M + H]$^+$.

{[Os(4-Cl-TPP)(CPh$_2$)]$_2$O} (4): This product was contaminated by 1,1,2,2-tetraphenylethylene ($C_{26}H_{20}$, the carbene coupling product of N_2CPh_2). Yield: 72%; ^{1}H NMR ($CDCl_3$): δ 8.53 (d, 8H, 8.10), 8.06 (s, 16H, H$_\beta$), 7.84 (d, 8H, 8.03), 7.50 (d, 8H, 8.10), 6.94 (d, 8H, 8.04), 5.68 (t, 4H, 7.25), 5.43 (t, 8H, 7.61), 1.13 (d, 8H, 7.58); ^{13}C NMR ($CDCl_3$): δ 269.94 (Os=C); UV/vis (CH_2Cl_2): λ_{max}/nm (log ε) 413 (5.06), 530 (4.14), 606 (sh, 3.88), 735 (3.86); IR (KBr): 1013 cm^{-1} (oxidation state marker band); Anal. Calcd for $C_{114}H_{68}Cl_8N_8OOs_2 \cdot 1/2C_{26}H_{20}$: C 63.66, H 3.28, N 4.68; Found: C 63.97, H 3.54, N 5.14; FAB MS: *m*/*z* 2231 [M + H]$^+$.

{[Os(4-Br-TPP)(CPh$_2$)]$_2$O} (5): Yield: 58%; ^{1}H NMR ($CDCl_3$): δ 8.45 (d, 8H, 8.03), 8.05 (s, 16H, H$_\beta$), 8.00 (d, 8H, 8.05), 7.65 (d, 8H, 8.04), 6.87 (d, 8H, 8.04), 5.68 (t, 4H, 7.18), 5.42 (t, 8H, 7.63), 1.12 (d, 8H, 7.12); ^{13}C NMR ($CDCl_3$): δ 270.06 (Os=C); UV/vis (CH_2Cl_2): λ_{max}/nm (log ε) 413 (5.16), 527 (4.25), 604 (sh, 3.99), 732 (3.91); IR (KBr): 1011 cm^{-1} (oxidation state marker band); Anal. Calcd for $C_{114}H_{68}Br_8N_8OOs_2$: C 52.96, H 2.65, N 4.33; Found: C 53.34, H 2.82, N 4.10; FAB MS: *m*/*z* 2587 [M + H]$^+$.

Preparation of [Os(TTP)(CPh$_2$)(py)] (6): A solution of **2** (50 mg, 0.024 mmol) and excess pyridine (ca. 10 mg) in benzene (20 ml) was refluxed for 20 h. Flash chromatography of the reaction mixture on an alumina column using dichloromethane/hexane (1:1 v/v) as eluent gave the desired product as a brownish red solid in 36% yield. The crystals suitable for X-ray structure determination were obtained by slow evaporation of a solution of **6** in dichloromethane-hexane at room temperature. ^{1}H NMR ($CDCl_3$): δ 7.76 (s, 8H, H$_\beta$), 7.71–7.68 (m, 8H), 7.42 (d, 4H, 6.95), 7.35 (d, 4H, 7.06), 6.49 (t, 2H, 7.36), 6.18 (t, 4H, 7.70), 3.89 (d, 4H, 7.96), the signals of bound pyridine: 6.46 (br, 1H), 5.80 (br, 2H), 2.76 (br, 2H); ^{13}C NMR ($CDCl_3$): δ 279.16 (Os=C); UV/vis (CH_2Cl_2): λ_{max}/nm 398 (Soret), 429 sh, 523, 551; IR (KBr): 1014 cm^{-1} (oxidation state marker band); Anal. Calcd for $C_{66}H_{51}N_5Os$: C 71.78, H 4.65, N 6.34; Found: C 71.32, H 4.34, N 6.52; FAB MS: *m*/*z* 1027 [M – Py + H]$^+$.

Intermolecular cyclopropanation of alkenes with ethyl diazoacetate (EDA) catalysed by 2. To a solution of **2** (1.03 mg, 0.5 μmol) and alkene (10 mmol) in dichloromethane (2 ml) was added a solution of EDA (57.05 mg, 0.5 mmol) in dichloromethane (10 ml) using syringe pump over 5 h at room temperature. The reaction mixture was stirred for an additional 1 h and then evaporated to dryness in vacuo. The *trans*:*cis* ratio was determined by GC-MS. The cyclopropyl ester products were purified by chromatography on a silica gel column with diethyl ether/hexane (1:5 v/v) as eluent.

Intramolecular cyclopropanation of allylic diazoacetates catalysed by 2. To a solution of **2** (1.03 mg, o.5 μmol) in dichloromethane (1 ml) was added a solution of allylic diazoacetate (1.0 mmol) in dichloromethane (10 ml) using syringe pump over

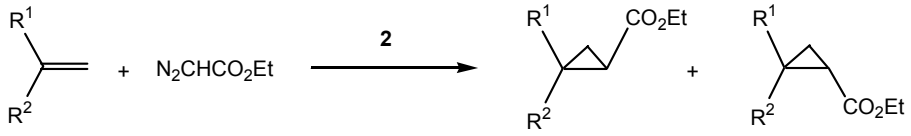
10 h at 40 ºC. The reaction mixture was stirred for an additional 1 h and then evaporated to dryness in vacuo. The bicyclic lactone thus obtained was purified by chromatography on a silica gel column with diethyl ether/hexane (1:5 v/v) as eluent.

C–H insertion reaction of cyclohexene with EDA catalysed by 2. To a solution of **2** (1.03 mg, 0.5 μmol) in cyclohexene (1 ml) was added a solution of EDA (0.25 mmol) in cyclohexene (7 ml) using syringe pump over 10 h at 60 ºC. The reaction mixture was further stirred for 1 h and then evaporated to dryness under reduced pressure. The products ethyl (cyclohexen-2-yl)acetate and 7-ethoxycarbonylbicyclo[4.1.0]heptane were purified by chromatography on a silica gel column with diethyl ether/hexane (1:5 v/v) as eluent and were identified as reported in the literature.[4]

References:

1. J. B. Miller, *J. Org. Chem.* 1959, **24**, 560.
2. M. P. Doyle, R. E. Austin, A. S. Bailey, M. P. Dwyer, A. B. Dyatkin, A. V. Kalinin, M. M. Y. Kwan, S. Liras, C. J. Oalmann, R. J. Pieters, M. N. Protopopova, C. E. Raab, G. H. P. Roos, Q.-L. Zhou, S. F. Martin, *J. Am. Chem. Soc*. 1995, **117**, 5763.
3. C.-M. Che, C.-K. Poon, W.-C. Chung, H. B. Gray, *Inorg. Chem*. 1985, **24**, 1277.
4. P. Müller, S. Tohill, *Tetrahedron* 2000, **56**, 1725.

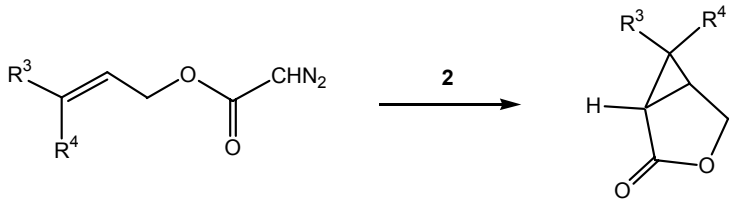
Table S1. Cyclopropanation of alkenes with EDA catalysed by **2**[a]



Entry	Alkene		Conversion of EDA (%)	Yield (%)[b] (*trans* + *cis*)	Ratio of *trans*:*cis*[c]
	R^1	R^2			
1	Ph	H	100	99	9.4:1
2	4-Cl-Ph	H	100	86	8.8:1
3	Ph	Ph	100	91	

[a] Reaction conditions: CH_2Cl_2, r.t., 5 h; **2**:EDA:alkene molar ratio = 1:1000:20000. [b] Based on consumed EDA. [c] Determined by GC-MS.

Table S2 Intramolecular cyclopropanation of allylic diazoacetates catalysed by **2**[a]



Entry	Substrate		Conversion (%)	Yield[b] (%)
	R^3	R^4		
1	Ph	H	90	63
2	H	C_2H_5	95	78
3	$Me_2C=CH(CH_2)_2$	Me	76	58

[a] Reaction conditions: CH_2Cl_2, 40 ºC, 10 h.; **2**:substrate = 1:2000 (molar ratio). [b] Based on consumed substrate.