Reactivity of Ruthenium 5,10,15,20-Tetramesitylporphyrin towards Diazoesters: Formation of Olefins†

J. P. Collman,*[a] E. Rose[b] and G. D. Venburg[a,c]

[a] Stanford University, Department of Chemistry, Stanford, CA 94305, USA

[b] Université Pierre et Marie Curie, Laboratoire de Chimie Organique, Tour 44, 4 Place Jussieu, 75252 Paris Cedex 05, France

[c] Abbott Laboratories, Department 91 J, Building AP9A, Abbott Park, IL 60064, USA

Ruthenium 5,10,15,20-tetramesitylporphyrin, Ru(tmp), reacts with 1 equiv. of N_2CHCO_2Et to afford the ethoxycarbonylcarbene [Ru(tmp)=CHCO_2Et] in the presence of an excess of N_2CHCO_2Et; the latter catalyses the formation of diethyl maleate as the major product at a rate of approximately one turnover per second.

The metalloporphyrin dimer complexes of Ru^{II} and Os^{II} [M(por)]₂ (M = Ru, Os; por = oep†, ttp†) have been proved to be interesting not only for the study of metal–metal bonds but also in the context of their reactions.[1,2] In this communication we report that the analogous monomeric tmp† Ru^{II} porphyrin[3a] complex catalyses the stereoselective decomposition of diazoesters to form olefinic products.

Six-coordinate [Ru(tmp)(L)(L')][3] complexes have been prepared using established procedures.[5] The amorphous [Ru(tmp)(MeCN)₂] obtained by a lyophilization procedure[2a,4] was pyrolysed under vacuum (10^{-5} Torr; 1 Torr = 133.3 Pa) at 230 °C to give a pure complex which has been previously reported to be a monomer, Ru(tmp).[3a]

Reaction of Ru(tmp) with ethylene affords the ethylene complex [Ru^{II}(tmp)($CH_2=CH_2$)]. Alternatively, this complex can be obtained either by reaction of [Ru(tmp)(L)₂] (L = MeCN, N₂, thf)[3] or [Ru(tmp)(thf)(N₂)][3b] with ethylene or by reaction of the reduced dianion Ru(tmp)[2] with CH_2Cl_2 or CH_2I_2.

Ru(tmp) reacts with ethyl diazoacetate to give cleanly and quantitatively the metalloporphyrin carbene complex [Ru^{II}(tmp)($CHCO_2Et$)]: eqn. (1). The split resonances of the ortho and meta substituents on the meso-aryl rings reveal the inequivalence of the two faces of the porphyrin ring. The integrals of the signals for the carbene substituents indicate the presence of one carbene fragment per metalloporphyrin. Note that the chemical shift for the α-carbon proton appears at a very low field [δ 13.79 (C_6D_6)].

$$Ru(tmp) + N_2CHCO_2Et \xrightarrow{C_6H_6} [Ru(tmp)=(CHCO_2Et)] \quad (1)$$
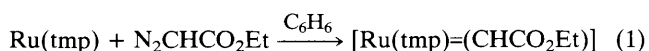
Ru(tmp) in the presence of an excess of ethyl diazoacetate in benzene or toluene at 25 °C under an inert atmosphere gives, in high yield, olefins resulting from the catalytic coupling of ethyl diazoacetate at a rate of approximately one turnover per second [eqn. (2)]. This coupling by Ru^{II} porphy-

$$Ru(tmp) + N_2CHCO_2Et \xrightarrow{-N_2} \quad (2)$$
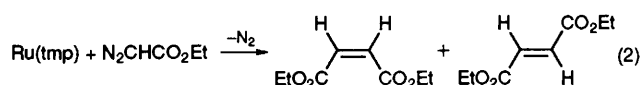
rins to form olefins proceeds through a metallocarbene intermediate, giving rise to an unexpected cis/trans ratio of 15 between diethyl maleate (the kinetic product) and diethyl fumarate (the thermodynamic product) in overall 91% yield (determined by GLC). A plausible mechanism for this reaction is suggested in Scheme 1. In comparison, a similar [Rh^{III}(tpp)I] species has been reported to catalyse slowly the decomposition of ethyl diazoacetate to form diethyl maleate in fair yield (37%).[6]

The [Ru(por)($CHCO_2Et$)] metalloporphyrin carbene complexes (por = oep, ttp, tmp) have been investigated for cyclopropanation activity with cyclohexene. Reaction conditions similar to those described in the Rh^{III} porphyrin[6] catalysed cyclopropanation reactions employing ethyl diazo-acetate and cyclohexene were used. In the presence of 1–10 equiv. of cyclohexene in benzene, the metalloporphyrin carbene complex [Ru(oep)($CHCO_2Et$)] does not react at room temp. nor at 60 °C. An axial ligand was added to attempt to induce cyclopropanation activity. The complexation of a strongly bound ligand may destabilize the carbene in the trans position and thus induce reactivity. Upon addition of 1 equiv. of PPh_3, the metallocarbene is transformed to [Ru(oep)(PPh₃)]. The only carbene products observed are the coupling products diethyl maleate and fumarate. No cyclopropanation products are observed.

In conclusion, our preliminary results show that Ru(tmp) catalyses the stereoselective decomposition of diazoesters to form mainly diethyl maleate.‡ This catalytic coupling of ethyl diazoacetate to olefins by a Ru^{II} porphyrin is to our knowledge the first example of a catalytic reaction that proceeds through a ruthenium metallocarbene intermediate.

---

‡ Preliminary results using [Ru(oep)]₂,[1] [Ru(ttp)₂][1] and [Os(oep)]₂ indicate that these catalysts are more active.[2] Turnover rates for these reactions are estimated based upon the length of time of N₂ evolution. Their turnover rates are conservatively estimated at 1–3 turnovers per second with a surprisingly similar rate with [Os(oep)]₂ compared with [Ru(oep)]₂. Little variance in the cis/trans ratio and olefin yield is noted between the different metalloporphyrins. Using the five-coordinate [Ru(oep)(PPh₃)] or the six-coordinate [Ru(oep)(PPh₃)₂] or [Ru(oep)(py)₂], the reactions are much slower. Note that we do not observe cyclopropanation reactions.[6] One report of production of olefins from substituted diazomethanes and osmium porphyrin carbene complexes appeared recently.[7]

All new compounds have been characterized by UV–VIS and NMR spectroscopies. The limited quantities of these metalloporphyrin complexes hindered their characterization by other methods. Bubbling C_2H_4 into Ru(tmp) gives an orange–red solution thought to be the bis-ethylene complex, which gives the darker red–brown monoethylene complex by bubbling N₂ through. [Ru(tmp)(C_2H_4)₂] ¹H NMR (C_6D_6) δ: H_β 8.60 (s, 8H); H_m 7.11 (s, 8H); p-Me 2.42 (s, 12H); o-Me 1.99 (s, 24H): UV–VIS (C_6H_6) λ_{max}/nm 412 (sh), 418 (Soret), 513, 546 (sh), 585; [Ru(tmp)(C_2H_4)] ¹H NMR in C_6D_6, δ: H_β 8.54 (s, 8H); H_m 7.13 (s, obscured by residual C_6H_6): p-Me 2.43 (s, 12H); o-Me 2.05 (s, 24H): in [²H₈]thf, δ: H_β 8.16 (s, 8H); H_m 7.24 (s, 8H); Me 2.55 (s, 12H); o-Me 1.94 (s, 12H); o'-Me 1.92 (s, 12H); $CH_2=CH_2$ – 3.76 (s, 4H); UV–VIS (C_6H_6) λ_{max}/nm 409 (Soret) 512; K₂Ru(tmp) ¹H NMR ([²H₈]thf) δ: H_β 8.40 (s, 8H), H_m 7.06 (s, 8H), p-Me 2.46 (s, 12H); o-Me 2.16 (s, 24H); UV–VIS (thf) λ_{max}/nm 316, 416 (Soret) 463, 586, 629; [Ru(tmp)($CHCO_2Et$)] ¹H NMR (C_6D_6) δ: H_β 8.55 (s, 8H); H_m 7.09 (s, 4H); $H_{m'}$ under residual benzene; p -Me 2.41 (s, 12H); o-Me 2.06 (s, 12H); o'-Me 1.97 (s, 12H); carbene CH 13.79 (s, 1H); CH₂ 2.58 (q, 2H, 7.1 Hz); Me 0.01 (t, 3H, 7.1 Hz); UV–VIS (C_6H_6): λ_{max}/nm 404 (Soret), 525 (v br); Ru (tmp) ¹H NMR (C_6D_6) δ: H_β 8.07 (s, 8H); H_m 7.20 (s, 4H, peak obscured by residual benzene); $H_{m'}$ 6.88 (s, 4H); p-Me 2.36 (s, 12H); o-Me 2.14 (s, 12H); o'-Me 1.15 (s, 12H) UV–VIS (C_6H_6): λ_{max}/nm 412 (Soret) 510.
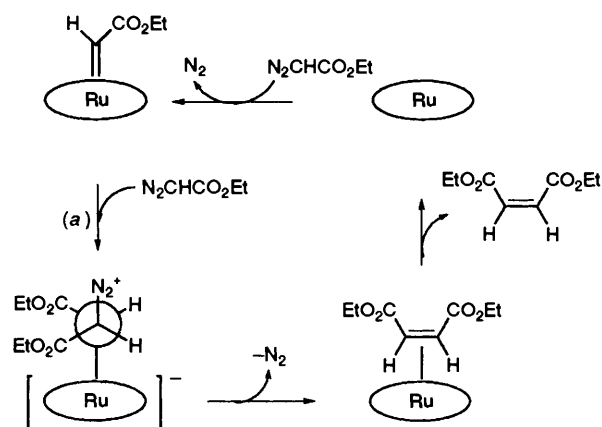
Scheme 1 Proposed mechanism and catalytic cycle for the Ru^{II} porphyrin catalysed coupling of ethyl diazoacetate. (*a*) The nucleophilic ethyl diazoacetate is proposed to attack the electrophilic carbene complex and produce an intermediate betaine-like species. Two different intermediates can be formed. We represent only one intermediate for reasons of clarity. The major conformation that leads to the less sterically crowded *cis* isomer is represented. *trans* Elimination of Ru(por) and N$_2$ is proposed to produce the olefin. The Ru(por) can react with additional equivalents of diazo compound to produce another equivalent of the carbene complex.

References

1 P. J. Brothers and J. P. Collman, *Acc. Chem. Res.*, 1986, **19**, 209; J. P. Collman, P. J. Brothers, L. McElwee-White and E. Rose, *J. Am. Chem. Soc.*, 1985, **107**, 6110; J. P. Collman, P. J. Brothers, L. McElwee-White, E. Rose and L. J. Wright, *J. Am. Chem. Soc.*, 1985, **107**, 4570.

2 Other metal–metal bonded dimers: (*a*) Mo, Os: J. P. Collman, C. E. Barnes and L. K. Woo, *Proc. Natl. Acad. Sci. USA*, 1983, **80**, 7684; (*b*) W, Re: J. P. Collman, J. M. Garner and L. K. Woo, *J. Am. Chem. Soc.*, 1989, **111**, 8141; (*c*) Rh: H. Ogoshi, J. Setsum and Z. Hoshida, *J. Am. Chem. Soc.*, 1977, **99**, 3869; J. Setsune, Z. Yoshida and H. Ogoshi, *J. Chem. Soc., Perkin Trans. 1*, 1982, 983; B. B. Wayland and A. Newmann, *Inorg. Chem.*, 1981, **20**, 3093; (*d*) Ir: K. J. Del Rossi and B. B. Wayland, *J. Chem. Soc., Chem. Commun.*, 1986, 1653.

3 (*a*) M. J. Camenzind, B. R. James and D. Dolphin, *J. Chem. Soc., Chem. Commun.*, 1986, 1137; (*b*) M. J. Camenzind, B. R. James, D. Dolphin, J. W. Sparapany and J. A. Ibers, *Inorg. Chem.*, 1988, **27**, 3054.

4 J. P. Collman, C. E. Barnes, P. N. Swepston and J. A. Ibers, *J. Am. Chem. Soc.*, 1984, **106**, 3500.

5 A. Antipas, J. W. Buchler, M. Gouterman and P. D. Smith, *J. Am. Chem. Soc.*, 1978, **100**, 3015.

6 H. J. Callot and E. Schaeffer, *Nouv. J. Chim.*, 1980, **4**, 311; H. J. Callot and C. Piechocki, *Tetrahedron Lett.*, 1980, **21**, 3489; H. J. Callot, F. Metz and C. Piechocki, *Tetrahedron*, 1982, **38**, 2365; see also the catalytic decomposition of diazo compounds by Cu^{II} salts, [Rh$_2$(OAc)$_4$] and [Rh^{III}(tpp)I] to form olefins, T. Oshima and T. Nagai, *Tetrahedron Lett.*, 1980, **21**, 1251; B. K. R. Shankar and H. Schechter, *Tetrahedron Lett.*, 1982, **23**, 2277; J. L. Maxwell, S. O'Malley, K. C. Brown and T. Kodadek, *Organometallics*, 1992, **11**, 645.

7 L. K. Woo and D. A. Smith, *Organometallics*, 1992, **11**, 2344; G. D. Venburg, PhD dissertation, Stanford University, 1990, in the case of the Os derivative.