





**Figure 1.** An ORTEP drawing of the molecular structure of (**3b**). Selected bond distances: Re(1)–Re(2) 3.057(2), Re(1)–C(3) 2.12(3), Ti–O(2) 2.02(2), Ti–C(5) 2.25(2), O(2)–C(3) 1.26(3), C(3)–C(4) 1.57(4), C(4)–C(5) 1.52(4) Å; angles: Re(2)–Re(1)–C(3) 176.7(7), Re(1)–C(3)–O(2) 125(2), Re–C(3)–C(4) 118(2), O(2)–Ti–C(5) 79.1(9), Ti–O(2)–C(3) 122(2), Ti–C(5)–C(4) 106(2), O(2)–C(3)–C(4) 117(2), C(3)–C(4)–C(5) 110(2)°.

The molecular structure of (**3b**) was further established by single-crystal X-ray diffraction. § Two molecules of (**3b**) with different conformations of the metallacyclic five-membered ring are crystallographically independent and make an enantiomorphic pair. The molecular structure of one of the two molecules is shown in Figure 1.

The carbenic ligand is *trans* to the Re–Re bond which contrasts with the complexes derived from  $\text{Re}_2(\text{CO})_{10}$  by conventional 'Fischer-type' methods where the carbene is *cis* to the Re–Re bond.<sup>3</sup> The C(3)–O bond distance in (**3b**) is considerably shorter than that of a usual C–O single bond, while the Ti–O bond is long. This shows that there is an important contribution from the dipolar resonance structure (**4**), as previously reported for zirconoxy-carbene-metal complexes.<sup>1</sup>

Since the compound (**1**) can be viewed as a titanacyclopentane complex,<sup>4,5</sup> the present reaction can be considered to proceed by a pericyclic  $[2_s + 2_s]$ -type reaction.<sup>4</sup> This can also be envisaged as a four-electron insertion process (migratory insertion) into a strained Ti–C  $\sigma$  bond. The observed reactivity of metal carbonyls toward (**1**) can be ascribed to the remarkable oxophilic nature of titanium.

§ *Crystal data for (3b)*: monoclinic, space group  $P2_1/a$ ,  $a = 30.401(1)$ ,  $b = 9.251(1)$ ,  $c = 27.561(5)$  Å;  $\beta = 105.73(1)^\circ$ ,  $U = 7460(2)$  Å<sup>3</sup>,  $D_c = 1.86$  g cm<sup>-3</sup>,  $M = 1044.98$ ,  $Z = 8$  (two independent molecules). Crystal of  $0.21 \times 0.32 \times 0.53$  mm was sealed in a thin-walled capillary tube under argon. Diffraction data were collected at  $-40^\circ\text{C}$  with monochromated Mo- $K_\alpha$  radiation,  $2\theta_{\text{max}} = 50^\circ$ . Intensities were corrected for absorption ( $\mu = 71.14$  cm<sup>-1</sup>). Unique 6715 reflections with  $|F_o| > 3\sigma(F_o)$  were used for the structure determination. The final conventional residual was  $R = 0.069$  and  $R_w = 0.082$  for 866 variables.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

When the complexes (**3a–e**) in  $[\text{D}_8\text{H}_8]$ toluene were kept at  $0$ – $30^\circ\text{C}$ , quantitative formation of ethylene and the corresponding metal carbonyls (**2a–e**) was observed, which indicates that the C(3)–C(4) bond of the oxatitanacyclopentane ring was selectively cleaved during the thermolysis. ¶ The fate of the titanocene moiety has not been established. Such fission of a C(carbenic)–C bond is unusual for Fischer-type carbene complexes.<sup>5</sup> This suggests that these complexes have chemical properties characteristic of metallacyclopentanes<sup>6–8</sup> and oxametallacyclopentanes<sup>9</sup> of group 4 transition metals.

Received, 10th March 1986; Com. 304

## References

- (a) G. Erker, U. Dorf, R. Benn, R.-D. Reinhardt, and J. L. Petersen, *J. Am. Chem. Soc.*, 1984, **106**, 7649; (b) G. Erker, U. Dorf, R. Mynott, Y.-H. Tsay, and C. Krüger, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 584.
- D. H. Berry, J. E. Bercaw, A. J. Jircitano, and K. B. Mertes, *J. Am. Chem. Soc.*, 1982, **104**, 4712.
- E. O. Fischer and P. Rustemeyer, *J. Organomet. Chem.*, 1982, **225**, 265.
- M. L. Steigerwald and W. A. Goddard, III, *J. Am. Chem. Soc.*, 1985, **107**, 5027.
- Recently, a similar novel bond fission was reported for the 1-oxacyclopent-2-ylidene-molybdenum complex: J. S. Drage and K. P. C. Vollhardt, *Organometallics*, 1986, **5**, 280.
- S. A. Cohen, P. R. Auburn, and J. E. Bercaw, *J. Am. Chem. Soc.*, 1983, **105**, 1136.
- S. A. Cohen and J. E. Bercaw, *Organometallics*, 1985, **4**, 1006.
- K. Mashima and H. Takaya, *Organometallics*, 1985, **4**, 1464.
- H. Takaya, M. Yamakawa, and K. Mashima, *J. Chem. Soc., Chem. Commun.*, 1983, 1283.

¶ The half lives of (**3a**), (**3b**), (**3c**), and (**3e**) in  $[\text{D}_8\text{H}_8]$ toluene are 116 (30°C), 223 (30°C), 73 (0°C), and 64 min (30°C), respectively.