



Scheme 2. Possible mechanistic steps involved in the formation of **4** from **6** and dppf.

The eight M–M contacts lie in the range 2.9922(13)–2.794(2) Å, the longest of which [Ru(1)–Ru(4)] is bridged by the phosphines of the dppf ligand. The carbido atom is displaced from the mean plane of the four metals that constitute the base of the pyramid by 0.218(12) Å, away from the apex [Ru(5)]. Along with the dppf ligand, 13 terminal carbonyls make up the ligand cage of the *nido*-cluster.

The dppf moiety is ligated in the *vicinal* form formally replacing two *axial* carbonyls of the known  $\text{Ru}_5\text{C}(\text{CO})_{15}$  cluster. The Ru–P bonds [Ru(1)–P(1), Ru(4)–P(2)] appear to be orientated such that they are ca. collinear with the apical to basal Ru–Ru contacts [Ru(1)–Ru(5), Ru(4)–Ru(5)]. The ferrocenyl group occupies a position proximal to the base of the cluster. The relative orientations of the P atoms with respect to the ferrocene moiety show a twist of 82.4°. The Cp rings are parallel to within estimated error, eclipsed to within 9.8° and produce an average distance of 1.658(6) Å from their centroids to the iron.

#### 2.4. The electronic spectra of **1**, **3** and dppf

The UV–vis spectra of metallocenes has proven to be a useful tool for probing subtle changes in electronic character of an encapsulated metal atom. The unusual green colour of **3** immediately suggested an electronic character significantly different to red **5**. Details of the electronic spectra and their interpretations for TM carbonyl clusters are unfortunately lacking in the literature. In this work the electronic spectra of **1**, **3** and dppf were measured in  $\text{CH}_2\text{Cl}_2$  solution at ambient temperature and the data are presented in Table 1, while relevant bond lengths and angles for **1** and **3** are presented in Tables 2 and 3, respectively.

The spectrum for dppf may be interpreted by comparison with that of ferrocene [29]. As shown in Fig. 4, the ground state electronic configuration of dppf may be taken to be  $(e_{2g})^4(a_{1g})^2$ , the HOMO being predominantly of  $d_{z^2}$  character. The maximum at 439 nm is assignable to the Laporte forbidden transition from the