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A Comparison of (*R*,*R*)-Me-DUPHOS and (*R*,*R*)-DUPHOS-*i*Pr Ligands in the Pd^0-Catalysed Asymmetric Allylic Alkylation Reaction: Stereochemical and Kinetic Considerations

Vanda Raquel Marinho,[a] J. P. Prates Ramalho,[a] Ana I. Rodrigues,[b] and Anthony J. Burke*[a]

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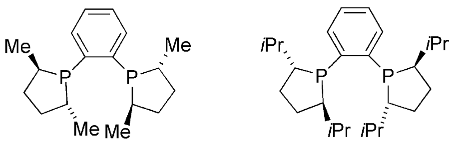
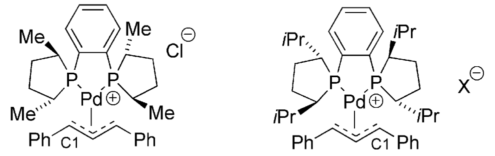
It has come to our attention that the absolute configuration shown for (*R,R*)-DUPHOS-*i*Pr (**1b**) shown in Figure 1 of the original article,[1] was in fact the (*S*,*S*) configuration and not the purported (*R*,*R*) absolute configuration. This is a consequence of the subtlety of the Cahn–Ingold–Prelog rules, a point that had previously been made by Burk et al.,[2] but had unfortunately been overlooked by us at the time of writing and of submitting this paper. Thus, Figure 1 should be as shown below.



1a **1b**

Figure 1. (*R*,*R*)-Me-DUPHOS (**1a**) and (*R*,*R*)-DUPHOS-*i*Pr (**1b**).

This therefore means that, in fact, complexes **2b** and **2c**, have the opposite absolute configuration to that shown as Figure 2 in our original paper (see the corrected version for Figure 2 below), and since the calculations on the Fukui function were inadvertently performed on the complex with the opposite absolute configuration to that used in the experiments (see Figure 4 in our original paper for the picture of the calculated structure), the preferred site of attack (C1) on the π-allyl complex **2b** (indicated as C1 in the corrected Figure 2) will give the malonate product with the (*R*) absolute configuration, as observed. Gratifyingly, this now explains on a very simple basis, the switch in the absolute configuration of the malonate product from (*S*) to (*R*) on going from (*R*,*R*)-DUPHOS-Me to (*R*,*R*)-DUPHOS-*i*Pr, and shows that, in both cases, it is the electronic effect and not any stereochemical effect, that is the controlling influence.



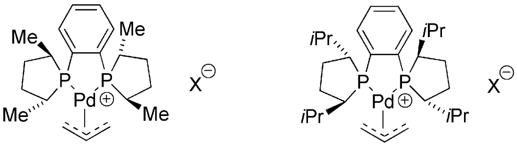
2a

2b X = Cl
2c X = OTf

Figure 2. Pd-allyl complexes **2**.

In our original paper, both the models shown in Figures 5 and 6 are incorrect as they depict the calculated structures of the complexes formed from the (*S*,*S*) enantiomer of DUPHOS-*i*Pr. These calculations now become redundant, as the switch in absolute configuration has now been explained (see above). Scheme 2 is also incorrect, as it depicts the wrong enantiomer of **2b**, but it suffices to give the general idea of the possible interconversions involved.

Figure 8 in our original paper should also be corrected as shown in the following Figure 8.



3a X = BF_4
4a X = Cl

3b X = BF_4
4b X = Cl

Figure 8. Isolated Pd-allyl complexes **3a** and **3b** formed using $AgBF_4$ and in situ formed complexes **4a** and **4b**.

The authors wish to apologise for any inconvenience this may have caused readers of our paper.

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[a] Departamento de Química and Centro de Química de Évora, Universidade de Évora,
Rua Romão Romalho 59, 7000 Évora, Portugal
Fax: +351-266745303
E-mail: ajb@dquim.uevora.pt
[b] Departamento de Tecnologia de Indústrias Químicas, Instituto Nacional de Engenharia, Tecnologia e Inovação,
Estrada do Paço do Lumiar, Edifício F, 1649-038 Lisboa, Portugal

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