Immobilisation of Ru-based metathesis catalysts and related aspects of olefin metathesis
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Keywords: Ruthenium / Carbene Complexes / Diphosphines / Olefin Metathesis

Abstract: A series of ruthenium benzylidene complexes containing diphosphines, e.g. xantphos, dppf, Cy$_2$P(CH$_2$)$_n$PCy$_2$ ($n = 5, 8$), has been prepared, either by phosphine exchange in the ruthenium carbene complex Ru(=CHPh)Cl$_2$(PPh$_3$)$_2$ or in a one-pot, two-step synthesis from RuCl$_2$(PPh$_3$)$_3$ and phenyldiazo methane. The complexes have been characterised spectroscopically (NMR, IR, MS) and by X-ray structural analysis. Their catalytic activity in the olefin metathesis is also discussed.
3.1 Introduction

In the past decade an impressive development of olefin metathesis catalysts and their applications has taken place, especially after the discovery of ruthenium carbene complexes of the general formula Ru(=CHR)Cl₂(PR')₂ [e.g. R = Ph; R' = Ph (1a) or Cy (1b)] by Grubbs and co-workers. A wide variety of ligands have been used for the preparation of new analogues of this type of catalyst. Some of these ligands, e.g. N-heterocyclic carbene complexes 1c, 1d, 1f, produce more active and versatile catalysts for alkene metathesis. In our group, 1b was selectively converted into a ruthenium carbene dimer that is active in the metathesis of internal alkenes.

Examples of neutral ruthenium carbene complexes containing a diphosphine ligand are scarce. Polystyrene-supported carbenes prepared by Nguyen and Grubbs might be considered as such. The exact structure of the immobilised ruthenium carbenes could not be determined, but most probably the ruthenium species resemble the structure of the homogeneous complex bearing the phosphine moieties trans to each other (1a-c). The catalytic activity of these immobilised catalysts was much lower than that of their homogeneous counterparts due to the detrimental effect of chelating diphosphine on the formation of the propagating ruthenium carbene species.

The group of Hoffmann performed exhaustive studies on ruthenium carbene complexes Haa and Hbb bearing the strained chelating diphosphines bis(di-tert-butylphosphino)methane and bis(di-tert-butylphosphino)ethane that coordinate in a cis-fashion to the metal centre. The neutral complexes containing these ligands are moderately active catalysts in ring opening metathesis polymerisation (ROMP) of norbornene and cyclooctene. Their dicationic dinuclear derivatives Hcc, obtained by chlorine abstraction with various silver salts,
are the best catalysts to date for ROMP of cyclooctene and they also catalyse ring closing metathesis (RCM) of 1,7-octadiene.\textsuperscript{5b} Recently, the structural and mechanistic aspects of their catalytic activity have been elucidated,\textsuperscript{5c} also with the help of mass spectrometry,\textsuperscript{7c} pointing at the mononuclear cationic species as responsible for very high activity of these systems.

Leitner and co-workers have demonstrated that the halide- and carbene-free Ru allyl complexes of type III with bidentate phosphines are efficient initiators for ROMP of norbornene.\textsuperscript{6} With the increasing length of the methylene bridge of the bidentate phosphine the content of trans double bonds increased in the polymer formed. These initiators failed to promote polymerisation of less strained monomers.

Recently, following our publication on the subject,\textsuperscript{7} several new articles have appeared dealing with ruthenium carbenes bearing bidentate phosphines. In the group of Fogg reactions of mixed phosphate species RuCl\textsubscript{2}(P\textsuperscript{2}P)(PPh\textsubscript{3}) with phenyldiazomethane PhCHN\textsubscript{2} were studied\textsuperscript{8a} for the following bidentate phosphines: 1,4-bis(diphenylphosphino)butane (dppb), 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (binap) and 1,4-bis(dicyclohexylphosphino)-butane (dcypb). The behaviour of a dinuclear complex [RuCl\textsubscript{2}(P\textsuperscript{2}P)]\textsubscript{2}, where P\textsuperscript{2}P is dppb, was also examined. The \textit{in situ} prepared carbenes of sort IVa show high activity in ROMP of norbornene, especially using the dinuclear complex, while no halide or phosphine abstraction is required. Polymers of relatively high molecular weight and narrow polydispersity are obtained. When a PPh\textsubscript{3}-free Ru source of formula RuCl(dcypb)(\mu-Cl)\textsubscript{3}Ru(dcypb)(N\textsubscript{2}) was used for the \textit{in situ} synthesis of the carbene IVa, again a very efficient catalytic system is produced.\textsuperscript{8b} The isolation of the carbenes formed was, however, not described. In a later paper from the same research group\textsuperscript{8c} the intrinsic instability of those carbenes is mentioned as the reason for their preparation \textit{in situ} instead of the isolation of pure compounds. The studies towards derivatives of the dcypb ligand starting from the dinuclear complex RuCl(dcypb)-(\mu-Cl)\textsubscript{3}Ru(dcypb)(N\textsubscript{2}) afforded isolable dinuclear monocarbenes of type IVb. Their activity in the ROMP of norbornene is reduced, compared to \textit{in situ} prepared mononuclear complex IVa of this ligand, which fact is attributed to the relative thermodynamic stability of the face-bridged Ru(\mu-Cl)\textsubscript{3}Ru species that manage only slow initiation.\textsuperscript{8c}
Ruthenium carbene complexes with pincer-type diphosphine ligands have been made by two research groups. Gusev and co-workers reacted ruthenium (and osmium) hydride RuHCl([L,3-(CH$_2$PMe$_2$)$_2$C$_6$H$_4$]) with 1-pentyne and tert-butylacetylene obtaining the carbene Va and vinyl-vinylidene Vb in which the pincer ligand acts as PCP-tridentate ligand. No report on the catalytic properties of such complexes was made. In the group of Fogg a closely related pincer ligand 1,3-(CH$_2$PCy$_2$)$_2$C$_6$H$_4$ was reacted with Ru(=CHCH=CMe)$_2$-Cl$_2$(PPh$_3$)$_2$ affording the complex Vc. The ligand is bidentate in this case with a possible agostic interaction of Ru with a proton of the phenylene ring. The complex was mentioned to be catalytically active though no experimental details have been provided.

Werner and co-workers have published the preparation of several ruthenium vinylidene, vinyl and carbene complexes with the bidentate phosphine 1,2-bis(dicyclohexylphosphino)ethane, e.g. complexes Vla and Vlb, including also carbene complex Vlc bearing 1,1'-bis(diphenylphosphino)ferrocene (dppf; see later for additional comments referring to Vlc). However, the complexes Vla and Vlc are inactive in the ROMP of cyclooctene.

Astruc and co-workers prepared two ruthenium carbenes Vlla, b bearing a chelating diphosphine PhCH$_2$N(CH$_2$PCy$_2$)$_2$ as model compounds for the preparation of carbenes supported on three generations of DAB-dendrimer (DAB = diaminobutane), e.g. Vllc (G1). Interestingly, the dendrimer supported carbenes Vllc promotes ROMP of norbornene much faster than Vlla (Vllb was inactive) giving also higher yields and higher molecular weights of polymer formed.
In order to expand the field of ruthenium carbenes containing diphosphines, we have prepared and structurally characterised ruthenium carbone complexes bearing diphosphines with flexible as well as with rigid backbones. Moreover, we studied their catalytic activity in the metathesis reaction of different kinds of alkenes.

3.2 Results and Discussion

3.2.1 Synthesis of Ruthenium Carbone Complexes Containing Diphosphines

For the preparation of the ruthenium carbone complexes we used two diphosphine ligands with rather rigid backbones, viz. xantphos (9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene) and dppf (1,1'-bis(diphenylphosphino)ferrocene). The first ligand has a rather large natural bite angle (calculated value: 111.7°). This could favour trans coordination of the phosphines to the ruthenium centre. The bite angle for dppf is much smaller and cis-coordination is generally preferred. Ruthenium benzylidenes complexes containing these diphosphines were prepared either by treatment of 1a with diphosphate that replaces the PPh$_3$ groups, or in a one-pot, two-step synthetic procedure from RuCl$_2$(PPh$_3$)$_3$, phenyldiazomethane and diphosphate in a similar way as described in the literature.

![Synthesis of Ruthenium Carbone Complexes Containing Diphosphines](image)

We obtained the ruthenium carbene complexes 2 and 3 in moderate to good yields via both procedures (see experimental part). Werner and co-workers obtained complex 3 (Vlc) in a higher yield starting from Grubbs catalyst 1b which is noteworthy since tricyclohexylphosphine (PCy$_3$), being more basic than PPh$_3$, is more difficult to substitute. When we reacted 1b with 1 equivalent of the xantphos ligand in CH$_2$Cl$_2$ for 20 h at rt, only 27% of 2 could be isolated, while the residue contained unreacted or decomposed 1b. This result discouraged us from using 1b as carbene source, also taking into consideration the atom economy of the overall process (sacrificing 2 equiv. of expensive PCy$_3$ ligand). In the solid state complexes 2 and 3 showed high stability towards oxygen and moisture. When dissolved in dichloromethane, complex 2 could even be passed through a short silica gel column.

![Solid state complexes 2 and 3](image)

We also prepared two diphosphine ligands in which the phosphorus atoms are connected via a flexible aliphatic chain, viz. 1,5-bis(dicyclohexylphosphino)pentane (4a) and 1,8-bis(dicyclohexylphosphino)octane (4b). Good yields were obtained by reaction of the
lithium salt of dicyclohexylphosphine with an appropriate dibromoalkane followed by crystallisation of the product.\textsuperscript{13}

\begin{align*}
\text{P-H} & \xrightarrow{1) \text{THF, n-BuLi}} \\
& \xrightarrow{2) \text{Br(CH}_2\text{)}_n\text{Br}} \\
& \text{n = 5, 8 dioxane}
\end{align*}

\[4a \ m = 1 \quad 4b \ m = 4\]

Reaction of 1a with the flexible ligands 4a and 4b according to the aforementioned procedures afforded pink products. The yields were moderate, mainly because of the formation of unidentified by-products, which did not contain a carbene moiety. We expected the formation of complexes similar to 2 and 3, and the initial data (NMR) of the complexes formed were in agreement with our expectations. Both X-ray analysis and molecular weight measurement in solution, however, showed that in fact the dimeric structures 5a and 5b had formed in which two ruthenium atoms are bridged by two ligand molecules in \( \mu \)-fashion (see section 3.2.3.3). MS spectra showed the molecular peaks of mass corresponding to the dinuclear species.

In the reaction of 1a with 2,3'-bis[(diphenylphosphino)methyl]-1,1'-biphenyl (2,3'-BISBI) the formation of unidentified by-products was observed. These impurities (~15%) could not be separated from the desired product 5c, which was obtained in 51% crude yield as a yellow-green solid. Nevertheless, only one carbene resonance was observed at 19.02 ppm as a triplet \( (J_{\text{PP}} = 7.8 \text{ Hz}) \) with the two methylene groups shifted downfield with respect to the free ligand (3.43 and 3.40 ppm in \( C_6\text{D}_6 \)) to 6.17 and 4.21 ppm and appearing as broad doublets \( (J_{\text{PP}} \approx 7.5 \text{ Hz}) \). In the \( ^{31}\text{P} \) NMR the phosphine resonances appeared as two strongly deformed doublets at 21.3 and 16.2 ppm of an AB spin system with a large \( ^2J_{\text{PP}} \) coupling constant of 314 Hz, suggesting a \( \text{trans} \) coordination of two inequivalent phosphine moieties. The calculated natural bite angle of 144° for the ligand consents such a coordination, keeping in mind the backbone flexibility range of circa \( \pm 25^\circ \).\textsuperscript{14} In our preparations we did not obtain any mononuclear ruthenium carbene complexes, neither with ligands 4a, 4b nor with a few other diphosphine ligands. In the case of bis(2-diphenylphosphinophenyl)ether (DPEphos) and 9,9-dimethyl-4,5-bis(diphenylphosphino)thioxanthene we observed decomposition of the carbene moiety. No reaction occurred when 1a was treated with 1,1'-bis(di-\text{tert}-butylphosphino)ferrocene, most probably because of the excessive steric bulk of tert-butyl moieties of the ligand.
3.2.2 Reactions with Trimethylsilyl Triflate

During attempts to prepare cationic derivatives of the described complexes by chloride abstraction using trimethylsilyl triflate,\(^5\) we only occasionally observed the formation of new carbenes species by NMR spectroscopy. Reaction of complexes 5a and 5b with 0.5 or 1 molar equivalent of \(\text{Me}_3\text{SiOTf}\) resulted in decomposition of the carbene unit and formation of unidentified products. The reaction of complex 2 with a three molar excess of \(\text{Me}_3\text{SiOTf}\) resulted in the products, which displayed two new carbene signals in the proton spectrum: at 18.95 ppm (\(J_{\text{PH}} = 6.0 \text{ Hz}\)) and 17.12 ppm (\(J_{\text{PH}} = 5.6 \text{ Hz}\)) in a 1:1 ratio. In the phosphorus spectrum two peaks were present at 46.1 and 42.1 ppm. Most probably an unsymmetrical dimer had formed, although its structure could not be assigned on the basis of only NMR spectra. Upon treatment with \(\text{Me}_3\text{SiOTf}\) complex 3 yielded a new carbene species appearing in proton NMR as triplet at 18.63 ppm (\(J_{\text{PH}} = 12.3 \text{ Hz}\)), while in phosphorus NMR a singlet was observed at 46.5 ppm. None of these products could be isolated in pure form and therefore only the crude reaction products were tested for activity in olefin metathesis.

3.2.3 Spectroscopic and Structural Characterisation

All isolated ruthenium complexes were spectroscopically characterised. The benzylidene proton in complexes 2 and 3, which bear phenyl groups on the phosphorus atoms, appeared as triplets. The coupling constant between the carbene proton and the phosphorus atoms of the coordinated phospine of complex 2 was similar to that of complex 1a and equal to 7.5 Hz. For complex 3 this value was 18.3 Hz, which is particularly large due to cis-coordination of phosphine moieties. In addition, the signal of the carbene proton was shifted upfield to 17.2 ppm, when compared to other carbene complexes, owing to the electron donating character of the ferrocene moiety and shielding of the carbene proton. The carbene signals in 5a and 5b showed no P-H coupling and appeared as singlets at ~20 ppm, similar to carbene complex 1b. The phosphines in these complexes are equivalent and they appeared as singlets in the \(^{31}\text{P}\) NMR spectrum. No relevant changes in the spectra of these complexes could be observed with low-temperature (to \(-60^\circ\text{C}\)) NMR studies. Mass spectrometry of the dinuclear complexes 5a and 5b revealed a fragmentation pathway in which the dimers fall apart into monomeric species with half the weight of the molecular ion. The structures of the carbene ruthenium complexes 2, 3 and 5a were confirmed by single-crystal X-ray analysis.

3.2.3.1 Crystal Structure of Complex 2.

The ruthenium centre in complex 2 is in a distorted octahedral environment; the \(\text{cis-}\)angles vary from 80.54(3)\(^\circ\) for O1-Ru-P2 to 102.56(6)\(^\circ\) for C1-Ru-P2; the bond lengths are between 1.8645(18) \(\text{Å}\) for Ru-C1 and 2.4042(4) \(\text{Å}\) for Ru-C11. The Ru-C1 bond distance is somewhat longer with respect to the \(p\)-chlorophenylcarbene analogue of complex 1b, which has a bond distance of 1.839 \(\text{Å}\).\(^2\) The P-Ru bond lengths in 2, viz, 2.3179(4) \(\text{Å}\) and 2.3519(4) \(\text{Å}\), are quite different. We assume that this difference is a steric consequence of the slightly twisted orientation of the benzylidene group, breaking the potential \(C_3\) symmetry of the molecule.
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Figure 1. Displacement ellipsoid plot of 2 drawn at the 50% probability level.

Hydrogen atoms and the dichloromethane solvent molecule are omitted for clarity. Relevant bond distances [Å] and angles [deg]: Ru-P1 2.3179(4), Ru-P2 2.3519(4), Ru-Cl1 2.4042(4), Ru-Cl2 2.3797(4), Ru-Cl1 1.8645(18), Ru-O 2.3314(12), Cl1-Ru-P1 87.089(15), Cl1-Ru-P2 88.467(15), Cl1-Ru-Cl2 165.145(16), Cl1-Ru-Cl1 101.05(6), P1-Ru-Cl1 96.41(6), P1-Ru-P2 161.021(17), Cl2-Ru-P1 88.603(16), Cl2-Ru-P2 91.025(16), Cl2-Ru-Cl1 93.55(6), P2-Ru-C1 102.56(6), Cl-Ru-O 175.90(6).

Compared to complex 5a (2.4014(4) Å and 2.4109(4) Å), the Ru-P bond lengths in 2 are significantly shorter suggesting that the ligand is more strongly coordinated to the metal. Structure 2 contains an additional Ru-O contact of 2.3314(12) Å. This distance is much longer than typically found for Ru-O bonds, which are normally 2.0-2.2 Å. We assume that the Ru-O contact in 2 is enforced by the strong phosphorus coordination of the diphosphine. Another indication of the relatively poor interaction between Ru and O is the non-planarity of the ligand. The interplanar angle between the aromatic rings of the xanthene backbone is 26.68(9)°, while in the free ligand this backbone is nearly flat (angle of ~ 3.4°).12
3.2.3.2 Crystal Structure of Complex 3.

In the case of complex 3 we see another feature. The Ru centre is five-coordinate and the coordination geometry is square pyramidal, distorted towards trigonal bipyramidal. More importantly, the phosphine moieties and chlorine ligands are cis-coordinated. The Ru-P bonds, viz, 2.2711(6) Å and 2.3106(6) Å, are even shorter than in complexes 2 and 5a, while the length of carbene bond (1.860(2) Å) remains virtually the same. The ferrocene moiety is essentially undistorted with parallel cyclopentadienyl rings and the phosphine substituents in an eclipsed conformation (torsion angle P1-C8-C13-P2 5.94(11)°).

![Figure 2. Displacement ellipsoid plot of 3 drawn at the 50% probability level.](image)

Hydrogen atoms and the dichloromethane solvent molecules are omitted for clarity. Relevant bond distances [Å] and angles [deg]: Ru-P1 2.2711(6), Ru-P2 2.3106(6), Ru-Cl1 2.4075(6), Ru-Cl2 2.3974(6), Ru-Cl 1.860(2), C11-Ru-P1 87.28(2), C11-Ru-P2 167.30(2), C11-Ru-Cl2 87.02(2), C11-Ru-Cl 101.92(7), P1-Ru-C1 88.81(7), P1-Ru-P2 95.37(2), Cl2-Ru-P1 146.80(2), Cl2-Ru-P2 83.97(2), Cl2-Ru-Cl 124.35(7), C1-Ru-P2 90.57(7).
As mentioned in the introduction, the same complex 3 (VIc) was independently made in the group of Werner. They also performed crystallographic analysis of the complex obtained in a similar manner as we did. Within the experimental error and differences in data acquisition, the two structure determinations are isostructural.

3.2.3.3 Crystal Structure of Complex 5a.

Complex 5a is a centrosymmetric dimer with the Ru atoms five-coordinate. The coordination geometries around the metal centres in 5a are nearly undistorted square-pyramidal with the phosphine moieties in trans positions. The bond lengths and angles are comparable to those observed in the p-chlorophenyl analogue of 1b.

**Figure 3.** Displacement ellipsoid plot of 5a drawn at the 50% probability level.

Hydrogen atoms are omitted for clarity. Symmetry operation: 1.5-x, 1.5-y, 1-z. Relevant bond distances [Å] and angles [deg]: Ru-P1 2.4014(4), Ru-P2 2.4109(4), Ru-Cl1 2.3885(4), Ru-Cl2 2.4060(4), Ru-Cl1 1.8392(17), Cl1-Ru-P1 89.585(13), Cl1-Ru-P2 88.234(14), Cl1-Ru-Cl2 163.144(15), Cl1-Ru-C1 107.93(5), P1-Ru-Cl1 97.83(5), P1-Ru-P2 168.721(14), Cl2-Ru-P1 90.875(13), Cl2-Ru-P2 88.034(14), Cl2-Ru-C1 88.70(5), C1-Ru-P2 93.37(5).
3.2.4 Metathesis Activity of Ruthenium Carbenes Bearing Diphosphines.

Table 1 shows the catalytic activity of the complexes in ROMP of norbornene (6), RCM of diethyl diallylmalonate (7) and self-metathesis of trans-4-decene (8) at room temperature (see experimental part). For comparison some literature data are also given.

![Chemical structures](image)

**Table 1. Metathesis activity of the ruthenium complexes 2, 3 and 5a-e.**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Alkene</th>
<th>Alkene:catalyst molar ratio</th>
<th>Time (h)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>6/7</td>
<td>100/20</td>
<td>no activity</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>100</td>
<td>4 (24)</td>
<td>43 (99)&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>20</td>
<td>no activity</td>
<td></td>
</tr>
<tr>
<td>5a</td>
<td>7</td>
<td>20</td>
<td>4 (24)</td>
<td>25 (77)</td>
</tr>
<tr>
<td>5b</td>
<td>7</td>
<td>20</td>
<td>4 (24)</td>
<td>33 (85)</td>
</tr>
<tr>
<td>5a</td>
<td>8</td>
<td>100</td>
<td>48</td>
<td>2</td>
</tr>
<tr>
<td>5b</td>
<td>8</td>
<td>100</td>
<td>48</td>
<td>3</td>
</tr>
<tr>
<td>5c&lt;sup&gt;e&lt;/sup&gt;</td>
<td>6</td>
<td>100</td>
<td>4 (20)</td>
<td>39 (92)</td>
</tr>
<tr>
<td>1a</td>
<td>6</td>
<td>100</td>
<td>1</td>
<td>99&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>1b</td>
<td>7</td>
<td>20</td>
<td>1</td>
<td>100</td>
</tr>
<tr>
<td>1b</td>
<td>8</td>
<td>550</td>
<td>4</td>
<td>36&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

a) Reactions conditions: room temperature, solvent CH<sub>2</sub>Cl<sub>2</sub>; catalyst concentration for ROMP of 6: 6.0 mM, for RCM of 7: 0.01 M, for self-metathesis of 8: 2.0 (or 3.0 for Ib) mM. b) Isolated yield 86%. c) Reaction done with impure material (of 85% purity); isolated yield 71%. d) Isolated yield 95% (ref. 2c). e) Ref. 15.

Complex 2 showed no metathesis activity, in contrast to internal oxygen-ruthenium chelate complexes<sup>16</sup> and Schiff-base-substituted ruthenium carbenes.<sup>3b</sup> This inactivity is probably due to the fact that a ruthenium-oxygen interaction is present in this complex along with two coordinated phosphorus atoms, so the ligand is tridentate and strongly bound to the metal (see section 3.2.3.1). Thus, the ruthenium atom is six-coordinated without a vacant coordination site, which makes the approach of any substrate impossible. Complex 3, containing a dppf ligand with phenyl substituents on phosphorus atoms, was only active in the ROMP of norbornene, but less so than complex 1a. According to Werner,<sup>10</sup> 3 (V1c) is inactive towards cyclooctene. The carbene 5c (of purity ~85%) with 2,3'-BISBI as ligand also displayed activity only in ROMP of norbornene converting 92% within 20 h. The dinuclear species with cyclohexyl moieties on the phosphorus atoms, 5a and 5b, showed activity in
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RCM of 7, although lower than catalyst 1b. They were only slightly active in metathesis of trans-4-decene after a prolonged reaction time.

The catalytic properties of all of the described complexes can be explained by consideration of the accepted mechanism of the metathesis reaction.\(^{17}\) The dissociation of one of the phosphine moieties is required in the initial steps of the reaction. The chelating effect of the bidentate ligand slows down this process. The uncoordinated arm of the ligand can exert some steric crowding in the ruthenium coordination sphere making the approach of the olefin more difficult.

The new ruthenium carbene species, observed in the products of chlorine abstraction reactions with Me\(_3\)SiOTf from complexes 2 and 3, did not display substantial activity in metathesis of the model alkenes. This observation is in contrast to a statement of Werner et al.\(^{10}\) on good ROMP activity towards cyclooctene of complex 3 after triflate addition (not supported by any experimental data). On the other hand, Amoroso and Fogg\(^{8a}\) found out that addition of chlorine scavenging AgPF\(_6\) to the in situ prepared cis-diphosphine carbene IVa, structurally closely related to 3, greatly retards the catalytic activity. Elucidation of this discrepancy would call for a more thorough examination.

3.3 Conclusions

Ruthenium carbene complexes containing diphosphines could be synthesised by either phosphine substitution in complex 1a or in a one-pot, two-step synthetic procedure starting from RuCl\(_2\)(PPh\(_3\))\(_3\), phenyldiazomethane and an appropriate phosphine. Diphosphines with rigid backbones produced mononuclear complexes, whereas the ligands featuring flexible aliphatic chains gave dinuclear complexes. These complexes are stable to air and moisture. They showed lower activity in ROMP of norbornene and RCM of diethyl diallylmalonate than catalysts 1a or 1b. This can be attributed to a detrimental effect of the chelating ligand, while also steric effects of the backbone may have contributed to the lower activity. Our observations are in agreement with the postulated mechanism for the metathesis reaction.

3.4 Experimental Part

All manipulations were performed using standard Schlenk techniques under an atmosphere of purified nitrogen. All solvents were purified by standard procedures.\(^{18}\) RuCl\(_2\)(PPh\(_3\))\(_3\),\(^{19}\) Ru(=CHPh)Cl\(_2\)(PPh\(_3\))\(_2\),\(^{2c}\) xantphos,\(^{12}\) 2,3'-'BISBI,\(^{14}\) and phenyldiazomethane solution\(^{20}\) were prepared according to literature procedures. Dicyclohexylphosphine (Strem), \(n\)-butyllithium solution in hexane (Acros) and dpff (Aldrich) were used as received. Norbornene (Acros) was purified by sublimation; diethyl diallylmalonate (Aldrich) and trans-4-decene (Fluka) were purified by passing them through activated alumina and distillation. Decane, 1,5-dibromopentane (Merck) and 1,8-dibromooctane (Merck) were purified by distillation. 2,3'-BISBI was made according to an unpublished procedure.\(^{14}\) All reagents were degassed through three continuous freeze-pump-thaw cycles. NMR spectra were measured with a Varian Mercury 300 spectrometer (at room temperature). Mass spectra were measured with a Jeol JMS SX/SX102A mass spectrometer. GC analyses were performed on a Carlo Erba 8000\(^{16}\) GC using a DB-5 (J&W Scientific) column. The determinations of the molecular weight in solution were done on a Hewlett Packard 302B vapour pressure osmometer.
3.4.1 Synthesis of Diphenylphosphines

Both compounds 4a and 4b were synthesised by reaction of dicyclohexylphosphine lithium salt (prepared by a slightly modified literature procedure) and an appropriate dibromoalkane, according to a modified literature procedure.

Preparation of 1,8-bis(dicyclohexylphosphino)octane (4b): 4.6 mL of a 2.4 M n-butyllithium solution in hexanes (~11 mmol) was added to a solution of dicyclohexylphosphine (2.03 mL, 10.1 mmol) in diethyl ether (20 mL) at RT. The reaction mixture was stirred for 10 minutes during which time a yellow precipitate of phosphine lithium salt was formed. The supernatant was taken out via cannula filtration and the solid was washed twice with ether (2×10 mL). Next, freshly distilled 1,4-dioxane (20 mL) was added causing dissolution of a certain amount of the salt. 1,8-Dibromo-octane (0.86 mL, 4.67 mmol) was added dropwise via a syringe. An immediate reaction occurred with dissolution of the solid and warming of the reaction mixture. It was refluxed for 10 minutes and formation of a white precipitate of a LiBrxCAC3 complex was observed. The precipitate was filtered off on a G4 filter, washed with ether and discarded. The combined solutions were then concentrated under vacuum and the formed white oil was dissolved in dry hot ethanol (15 mL). The solution was left overnight at 0°C for crystallisation. The crystallisation procedure was repeated, and a white solid (1.84 g, yield 81%) was obtained. 1H NMR (CDCl3): δ (ppm) 2.00–1.05 (m). 13C{1H} NMR (CDCl3): δ (ppm) 34.39 (d, J = 14.7 Hz), 32.40 (d, J = 11.0 Hz), 31.23 (d, J = 14.6 Hz), 30.25 (s), 29.85 (d, J = 8.2 Hz), 29.52 (d, J = 20.8 Hz), 28.08 (pseudo t, Japp = 3.7 Hz), 27.37 (s), 22.44 (d, J = 18.3 Hz). 31P{1H} NMR (CDCl3): δ (ppm) -4.85 (s). FAB-MS: m/z (rel. intensity, %): 507 ([M+H]+, 80), 506 ([M]+, 18), 505 ([M-H]+, 50), 423 ([M-Cy]+, 100), 341 ([M-2Cy+H]+, 25), 309 (73), 267 (10), 225 (13), 130 (15), 115 (20), 78 (40), 76 (32), 55 (50), 41 (20).

Experimental data for 1,5-bis(dicyclohexylphosphino)pentane (4a): Starting from 2.02 mL (10.1 mmol) of dicyclohexylphosphine and 1,5-dibromopentane (0.68 mL, 0.50 mmol) a white solid was obtained in a yield of 65% (1.36 g). 1H NMR (CDCl3): δ (ppm) 2.05–1.10 (m). 13C{1H} NMR (CDCl3): δ (ppm) 34.31 (d, J = 14.6 Hz), 31.18 (d, J = 14.6 Hz), 29.77 (d, J = 8.5 Hz), 29.21 (d, J = 19.6 Hz), 28.08 (pseudo t, Japp = 3.8 Hz), 27.32 (s), 22.25 (d, J = 18.3 Hz). 31P{1H} NMR (CDCl3): δ (ppm) -4.82 (s). FAB-MS: m/z (rel. intensity, %): 465 ([M+H]+, 85), 464 ([M]+, 10), 463 ([M-H]+, 45), 381 ([M-Cy]+, 100), 299 ([M-2Cy+H]+, 30), 267 (88), 153 (15), 83 (35), 81 (25), 41 (15). Anal. Calc'd for C25H32P2C: C, 74.96; H, 11.71. Found: C, 74.69; H, 11.78.

3.4.2 Synthesis of Ruthenium Carbene Complexes

Ru(C=CHPh)Cl2(xantphos) (2): Complex 1a (0.256 g; 0.325 mmol) was dissolved in dichloromethane (20 mL) and the solution was cooled to -78°C. The xantphos ligand (0.171 g, 0.295 mmol) was added as a solution in dichloromethane (5 mL) via a syringe. The reaction mixture was stirred for 15 minutes at -78°C, then allowed to warm to RT and stirred for 2 h. The mixture was then concentrated and a green precipitate was formed upon addition of pentane (20 mL). The brownish liquor was discarded and the solid was washed with pentane. It was redissolved in dichloromethane and reprecipitated. The reaction yielded 0.23 g (92%) of a green microcrystalline solid. 1H NMR (CD2Cl2): δ (ppm) 19.08 (t, JHH = 7.5 Hz, 1 H, Ru=C=CHPh), 7.92 (d, JHH = 7.6 Hz, 2 H, CH of xanthene), 7.78 (d, JHH = 7.5 Hz, 2 H, CH of xanthene), 7.59-7.23 (m, 25 H, 5 × Ph), 7.08 (t, JHH = 7.5 Hz, 2 H, CH of xanthene), 1.82 (s, 6 H, CH3). 13C{1H} NMR (CD2Cl2): δ (ppm) 320.59 (t, J = 10.6 Hz, Ru=C=CHPh), 155.62 (t, J = 4.0 Hz), 154.39 (t, J = 7.3 Hz), 135.45, 134.91 (t, J = 5.5 Hz), 132.68,
131.41 (d, J = 45 Hz), 131.18 (d, J = 46 Hz), 131.09 (d, J = 47 Hz), 130.22, 129.17, 128.02 (t, J = 4.9 Hz), 125.37, 123.31 (t, J = 18.9 Hz), 35.19 (C(CH$_3$)$_3$), 33.52 (CH$_3$). **$^{31}$P{H} NMR (CD$_2$Cl$_2$):** δ (ppm) 36.26 (s). **IR (KBr):** (cm$^{-1}$) 3056 (m), 2953 (w), 2918 (w), 1481 (w), 1436 (s), 1399 (vs), 1260 (w), 1213 (m), 1194 (m), 1094 (m), 877 (w), 743 (m), 693 (s), 522 (s), 505 (m). **FD-MS:** m/z (rel. intensity, %): 840 ([M]$^+$, 100), 820 (15), 611 (5), 353 (97); isotopic pattern for [C$_6$H$_3$Cl$_2$OP$_2$Ru]$^+$: m/z (calcd intensity, found intensity): 834 (10, 20), 835 (5, 12), 836 (11, 24), 837 (28, 44), 838 (39, 59), 839 (62, 80), 840 (100, 100), 841 (66, 82), 842 (96, 95), 843 (45, 63), 844 (40, 61), 845 (16, 28), 846 (7, 28), 847 (2, 17), 848 (1, 6). **Anal.** Calcd for C$_6$H$_3$Cl$_2$OP$_2$Ru: C, 65.71; H, 4.56. Found: C, 64.92; H, 4.69.

**Ru(=CPh)Cl$_2$(dppf):** To a cooled to -78°C solution of 1a (0.235 g; 0.30 mmol) in dichloromethane (30 mL), a solution of dppf (0.166 g; 0.30 mmol) in dichloromethane (5 mL) was added via a syringe. The reaction mixture was stirred for 20 minutes at -78°C. Then it was allowed to warm to room temperature and the colour of the mixture changed to brown. After 1 h most of the solvent was evaporated and a greenish solid was precipitated with pentane (25 mL). The orange solution was discarded and the solid was washed a few times with pentane, reprecipitated twice from dichloromethane and then dried under vacuum. 0.123 g (50%) of a green-brown microcrystalline product was obtained. **$^1$H NMR (CD$_2$Cl$_2$):** δ (ppm) 17.20 (t, J$_{HH}$ = 18.3 Hz, 1 H, Ru=CHPh), 8.66 (d, J$_{HH}$ = 7.7 Hz, 2 H, o-CH$_{arom}$), 7.92-6.95 (m, 23 H, CH$_{arom}$), 4.78, 4.60, 4.48, 4.37 (4 x s, 4 x 2 H, CH of Cp). **$^{13}$C{H} NMR (CD$_2$Cl$_2$):** δ (ppm) 303.06 (t, J$_{CH}$ = 17.4 Hz, Ru=CHPh), 151.06, 136.21 (t, J = 5.1 Hz) 133.70 (t, J = 4.9 Hz), 133.38, 131.40 (2 C), 130.03 (2 C), 128.39 (t, J = 4.9 Hz), 127.75 (t, J = 5.2 Hz), 75.16 (4 C), 73.33 (2 C, t, J = 3.6 Hz), 70.14 (2 C). **$^{31}$P{H} NMR (CD$_2$Cl$_2$):** δ (ppm) 51.95 (s). **IR (KBr):** (cm$^{-1}$) 3054 (m), 1434 (s), 1249 (m), 1178 (m), 1161 (m), 1094 (s), 1038 (m), 874 (w), 826 (w), 744 (s), 693 (s), 631 (w), 562 (m), 511 (s), 476 (m). **FD-MS:** m/z (rel. intensity, %): 816 ([M]$^+$, 100), 780 (20), 726 (5), 689 (5), 586 (10), 554 (8); isotopic pattern for [C$_4$I$_2$H$_3$Cl$_2$FeP$_2$Ru]$^+$: m/z (calcd intensity, found intensity): 808 (1, 2), 809 (0.5, 1), 810 (10, 18), 811 (6, 14), 812 (13, 15), 813 (31, 32), 814 (43, 45), 815 (63, 75), 816 (100, 100), 817 (63, 67), 818 (92, 92), 819 (41, 51), 820 (38, 41), 821 (14, 23), 822 (7, 12), 823 (2, 4). **Anal.** Calcd for C$_4$I$_2$H$_3$Cl$_2$FeP$_2$Ru=CH$_2$Cl$_2$: C, 55.98; H, 4.08. Found: C, 55.96; H, 4.02.

**Cl$_2$(PhHC=)Ru[m-(C$_5$H$_4$P(3CH$_3$PCH$_3$)$_3$)]Ru(=CPh)Cl$_2$ (5b):** RuCl$_2$(PPh$_3$)$_3$ (1.44 g, 1.50 mmol) was dissolved in dichloromethane (50 mL) and the solution was cooled to -50°C. A cooled solution (0°C) of phenylidiazomethane (~ 2 molar excess) was added via a polyethylene cannula over 10 min. The mixture was allowed to warm to -30°C and a 1.1 molar excess (0.88 g) of diphenosphine 4b was added. The reaction mixture was allowed to warm to room temperature and subsequently stirred for 30 min. Next, most of the solvent was evaporated leaving a dark-red oil. Ethanol (30 mL) was added and the mixture was vigorously stirred. A dark-red precipitate was formed, which was separated from the liquor, redissolved in DCM and reprecipitated with ethanol. The red-pink solid thus obtained was washed with cooled dichloromethane (10 mL) and dried, giving a pink solid. The remaining liquor was concentrated to a few millilitres and left overnight at -20°C. The crystallised dark-pink solid was filtered, washed with cold dichloromethane and dried. The combined yield of the product was 0.392 g (34%). **$^1$H NMR (CD$_2$Cl$_2$):** δ (ppm) 20.00 (s, 1 H, Ru=CHPh), 8.52 (d, J$_{HH}$ = 7.8 Hz, 2 H, o-CH$_{arom}$), 7.84 (t, J$_{HH}$ = 7.5 Hz, 1 H, p-CH$_{arom}$), 7.56 (t, J$_{HH}$ = 7.8 Hz, 2 H, m-CH$_{arom}$), 2.40-0.63 (m, 60 H, all CH$_{alil}$). **$^{13}$C{H} NMR (CD$_2$Cl$_2$):** δ (ppm) 297.6 (Ru=CHPh), 155.9, 131.1, 130.8, 130.0, 33.0 (m), 30.2, 29.7, 29.3, 28.1 (pseudo t, J$_{app}$ = 6.4 Hz), 26.9, 26.1, 25.3, 18.4. **$^{31}$P{H} NMR (CD$_2$Cl$_2$):** δ (ppm) 33.46 (s). **IR (KBr):** (cm$^{-1}$) 3060 (w), 2972 (vs), 2851 (s), 1903 (w), 1446 (m), 1243
(w), 1173 (w), 1117 (w), 1005 (w), 892 (w), 851 (w), 743 (m), 689 (w), 515 (w). **FD-MS:** *m/z* (rel.
intensity, %) 1536 ([M]+, 66), 768 ([M/2]+, 74), 638 (55), 507 (100, [Cy2P(CH2)3PCy2]+), 254 (61). **Anal.** Caled for Cy7H12Cl2P3Ru2: C, 60.92; H, 8.65. Found: C, 60.35; H, 8.70. Molecular weight
determination in CH2Cl2 showed the complex to be still dinuclear in the solution.

**Cl2(PhHC=)Ru[µ-(Cy2P(CH2)3PCy2)]2Ru(=CHPh)Cl2 (5a):** The reaction was carried out as
descrribed for 5b, starting from 1.218 g (1.25 mmol) of RuCl2(PPh3), phenyldiazomethane solution
(~2 molar excess) and 0.660 g (1.40 mmol) of diphosthene 4a. A pink-brown solid was isolated (0.290 g,
32% yield) upon repeated precipitation from dichloromethane solution with ethanol. **1H NMR**
(CD2Cl2): δ (ppm) 19.89 (s, 1 H, Ru=CHPh), 8.52 (d, JH H = 7.7 Hz, 2 H, o-CH2CH2), 7.60 (t, JHH = 7.2
Hz, 1 H, p-CH2CH2), 7.36 (t, JHH = 7.6 Hz, 2 H, m-CH2CH2), 2.40-0.83 (m, 54 H, all CH2CH). **13C{1H}
NMR (CD2Cl2): δ (ppm) 296.9 (Ru=CHPh), 151.3, 130.3, 129.8, 129.2, 34.1, 33.0 (pseudo t), 29.3 (d,
J = 17.2 Hz), 27.9, 26.9, 24.5, 18.7. **31P{1H} NMR** (CD2Cl2): δ (ppm) 30.40 (s). **IR** (KBr): (cm−1) 3057
(w), 2926 (vs), 2850 (vs), 2105 (w), 1933 (w), 1901 (w), 1446 (s), 1329 (w), 1262 (m), 1241 (m),
1173 (m), 1026 (m), 1005 (m), 891 (m), 850 (m), 818 (m), 742 (m), 690 (m), 515 (w). **FD-MS:** *m/z*
(rel. intensity, %) 1453 ([M-H]+, 12), 1249 (30), 727 ([M/2]+, 22), 637 (85), 599 (100), 572 (54), 481
(27), 258 (23). **Anal.** Caled for Cy7H12Cl2P3Ru2: C, 59.49; H, 8.32. Found: C, 58.90; H, 8.27.
Molecular weight determination in CH2Cl2 showed the complex to be dinuclear also in the solution.

**Ru(=CHPh)Cl2(2,3’-BISBI) (5e):** The reaction of 1a with 2,3'-bis((diphenylphosphino)-
methyl)-1,1’-biphenyl (2,3'-BISBI) was performed as for complex 3, to give in 51% crude yield a
yellow-green solid after two recrrippitations. An unidentifled impurity (~15%, indicated by **31P NMR**)
was still observed, which could not be separated from the wanted product 5e. **1H NMR** (CD2Cl2): δ
(ppm) 19.02 (t, JPH = 7.8 Hz, 1 H, Ru=CHPh), 8.95 (s, 1 H, CH2CH2), 7.90-6.92 (m, ~30 H,
CH2CH2), 6.17 (d, JHY=7.5 Hz, 2 H, CH2P), 4.21 (d, JYP=7.5 Hz, 2 H, CH2P). **31P{1H} NMR** (CD2Cl2): δ
(ppm) 26.0 (s, impurity), 21.3 & 16.2 (d, 2 JPP = 314 Hz, 2 P in trans fashion).

### 3.4.3 Treatment of New Ru Carbene Complexes with Trimethylsilyl Triflate

The experiments were carried out as described in the literature,2b usually with a three molar
excess of Me3SiOTf added to a dichloromethane solution of ruthenium complex at −78°C. The reaction mixture was stirred for 1 h at room temperature. The product was isolated by repeated
precipitation from dichloromethane solutions using pentane.

### 3.4.4 Metathesis Experiments

**ROMP of norbornene.**2b In a typical experiment, a stock mixture of norbornene (6) and decane
(as internal standard for GC analysis) was used. An aliquot of this solution (116 mg of norbornene,
1.23 mmol) was added via a syringe to the solution of ruthenium compound 3 (9.5 mg, 12.1 μmol) in
dichloromethane (2 mL) at room temperature. The resulting concentration of catalyst and norbornene
were 0.006 M (1 equiv.) and 0.60 M (100 equiv.), respectively. The viscous mixture was stirred for 24
h, while occasionally samples were taken and analysed by GC. Next, the mixture was exposed to air,
and dichloromethane (4 mL) with traces of ethyl vinyl ether to quench the reaction was added. The
mixture was stirred for another 20 minutes, filtered through a short column of silica gel and poured
into vigorously stirred methanol. A white, tacky polymer precipitated, which was washed several
times with methanol and dried under vacuum; the yield using catalyst 3 was 98 mg (86%).
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**RCM of diethyl diallylmalonate.** In a typical experiment, the diene 7 (0.120 mL, 0.50 mmol) was added to 12.5 μmol (19.2 mg, 5 mol% of carbene moiety) of the ruthenium catalyst 5b in dichloromethane (2.5 mL) at room temperature. The progress of the reaction was followed by GC.

**Self-metathesis of trans-4-decene:** In a typical experiment, trans-4-decene (8, 0.19 mL, 1.0 mmol) was added to a solution of 5a (7.1 mg, 4.9 μmol, 1 mol% of carbene moiety) in dichloromethane (2.5 mL) at room temperature. The resulting solution was vigorously stirred. The progress of the reaction was followed by GC.

### 3.4.5 X-ray Structure Determinations

Crystals of complexes 2 and 3 were grown from mixture of n-hexane/CH₂Cl₂ (1/1 v/v) at 2°C and in case of complex 5a from CH₂Cl₂. X-ray intensities were measured on a Nonius KappaCCD diffractometer with rotating anode (λ=0.71073 Å) at a temperature of 150(2) K.

**Table 2.** Summary of data for the crystal structure analysis of 2, 3 and 5a.

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<tr>
<td>2</td>
<td>C₆₄H₃₈Cl₂OP₂Ru + CH₂Cl₂</td>
<td>925.60</td>
<td>Green</td>
<td>0.48 x 0.15 x 0.15</td>
<td>Triclinic</td>
<td>P 1 (No. 2)</td>
<td>11.0320(2)</td>
<td>11.1015(2)</td>
<td>17.7959(3)</td>
<td>89.7781(9)</td>
<td>81.1990(10)</td>
<td>70.8813(10)</td>
<td>2032.54(6)</td>
<td>2</td>
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<td>Platon (Mulabs)</td>
<td>0.82-0.90</td>
<td>47590 / 9233</td>
<td>502 / 0</td>
<td>0.0275 / 0.0649</td>
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<tr>
<td>3</td>
<td>C₄₁H₄₈Cl₂FeP₂Ru + 2xCH₂Cl₂</td>
<td>986.29</td>
<td>Brown</td>
<td>0.51 x 0.27 x 0.18</td>
<td>Monoclinic</td>
<td>P2₁/c (No. 14)</td>
<td>13.9971(1)</td>
<td>14.6922(1)</td>
<td>20.0647(1)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>4078.94(5)</td>
<td>4</td>
<td>1.606 / 1.229</td>
<td>Platon (Mulabs)</td>
<td>0.70-0.81</td>
<td>87477 / 9342</td>
<td>514 / 0</td>
<td>0.0314 / 0.0803</td>
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<tr>
<td>5a</td>
<td>C₇₂H₁₂₀Cl₄P₄Ru₂ + solvent</td>
<td>1453.50 [*]</td>
<td>Red</td>
<td>0.30 x 0.30 x 0.12</td>
<td>Monoclinic</td>
<td>C2/c (No. 15)</td>
<td>24.2122(3)</td>
<td>27.8321(4)</td>
<td>14.3627(2)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>9138.0(2)</td>
<td>4</td>
<td>1.057 / 0.549 [*]</td>
<td>Platon (Mulabs)</td>
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<td>53789 / 10470</td>
<td>374 / 0</td>
<td>0.0283 / 0.0746</td>
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</table>

[*] The contribution of the disordered solvent was not taken into account for the calculation of Fw, ρ, and μ (see text in experimental section).
Structures 2 and 5a were solved with automated Patterson methods (DIRDIF97); structure 3 was solved with direct methods (SIR97). The structures were refined with SHELXL-97 against F² of all reflections. Structure 5a contains large voids (2571.8 Å³/unit cell) filled with disordered dichloromethane molecules. Their contribution to the structure factors was secured by back-Fourier transformation (program PLATON, CALC SQUEEZE, 615 e⁻/unit cell). Structure calculations, structure drawings and checking for higher symmetries were performed with the PLATON package. Further information regarding the crystal structure determinations is given in Table 2.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 147124 (2), 147125 (3) and 147126 (5a). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

3.5 Acknowledgements and References

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14 M. Kranenburg, P. W. N. M. van Leeuwen, personal communication.


