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A Stable Ruthenium Catalyst for Productive Olefin Metathesis

Grant S. Forman,[*,†] Ann E. McConnell,[†] Martin J. Hanton,[†]
Alexandra M. Z. Slawin,[‡,§] Robert P. Tooze,[†] Werner Janse van Rensburg,[‖]
Wolfgang H. Meyer,[‖,⊥] Cathy Dwyer,[‖] Megan M. Kirk,[‖] and
D. Wynand Serfontein[‖]

*Sasol Technology Research Laboratory, St Andrews, Sasol Technology (UK) Limited,
Purdie Building, North Haugh, St Andrews, Fife KY16 9ST, Scotland, U.K., School of
Chemistry, University of St Andrews, Purdie Building, North Haugh, St Andrews,
Fife KY16 9ST, Scotland, U.K., and Sasol Technology Research & Development, PO Box 1,
Klasie Havenga Road, Sasolburg, 1947, South Africa*

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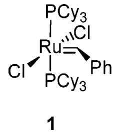
*Summary: New ruthenium carbene complexes **5** and **6**, containing a rigid bicyclic phosphine moiety, have been prepared, and the structure of **5** has been unambiguously established by single-crystal X-ray diffraction studies. These ruthenium-based complexes show excellent stability to air and moisture, can be recycled by chromatography, and are available from simple precursors. They are efficient catalysts for various metathesis reactions, particularly for applications where high selectivity is required.*

Ruthenium alkylidene complexes have attracted significant attention in recent years as efficient catalysts for olefin metathesis and have rapidly evolved into versatile tools for organic and polymer chemistry.[1] Attempts to improve the stability and overall performance of the ruthenium benzylidene complex $[(PCy_3)_2(Cl_2)Ru{=}CHPh]$ (**1**)[2] have been mainly focused on the development of N-heterocyclic carbene-coordinated ruthenium complexes such as $[(H_2IMes)(PCy_3)(Cl_2)Ru{=}CHPh]$ (**2**),[3] which are reported to display dramatically increased reactivity with a wide variety of olefin substrates.[4] The high activity and broad application profile of ruthenium alkylidene metathesis catalysts can be offset by the propensity toward decomposition at low catalyst loadings,[5] particularly for ring-closing metathesis (RCM) and cross-metathesis (CM) reactions. To successfully apply homogeneous metathesis to the industrial-scale production of commodity olefins, both high turnover numbers and selectivities are required.[6]



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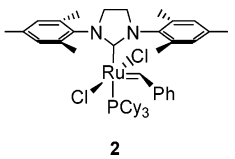

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In this context, the Grubbs first-generation catalyst **1** is generally incompatible with olefin feedstocks derived from Fischer−Tropsch[7] conversion of synthesis

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[*] To whom correspondence should be addressed. E-mail: grant.forman@sasol.com.

[†] Sasol Technology (UK) Limited.

[‡] University of St. Andrews.

[§] Fax: +44 (0) 1334 463 384. Tel: +44 (0) 1334 467 280. E-mail: amzs@st-andrews.ac.uk.

[‖] Sasol Technology Research and Development.

[⊥] Fax: +27 11 5223593. Tel: +27 16 960 4443. E-mail: wolfgang.meyer@sasol.com.

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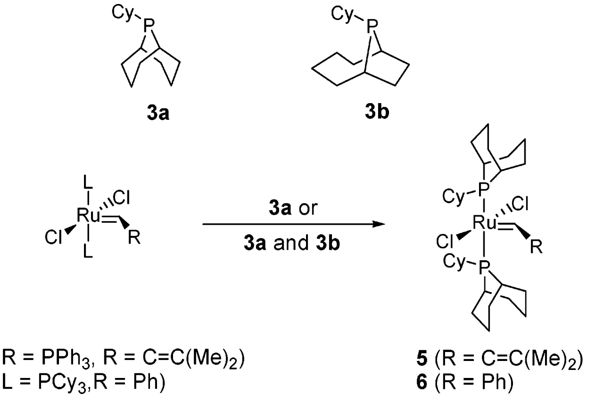
gas, since it displays poor thermal stability and short lifetimes at low catalyst loadings. For example, complex **1** has a lifetime of only ca. 15 min for the self-metathesis (SM) of 1-octene at 50 °C (S/C = 20 000:1). While the N-heterocyclic carbene (NHC) complex **2** displays significantly enhanced activity relative to **1**, olefin isomerization[5d,8,9] is a competitive and complicated process, often resulting in poor overall selectivity.

On the basis of the foregoing, we have focused our attention on developing improved first-generation olefin metathesis catalysts that are more likely to give selective reactions. Phosphine substitution has already been studied extensively by Grubbs and co-workers,[2d] and tricyclohexylphosphine (PCy_3) was determined to be an optimal ligand. However, with one notable exception,[10] since the advent of NHC-containing ruthenium olefin catalysts, relatively little effort has been devoted toward further developing ruthenium-based catalysts containing two phosphine donor ligands.[11]

We recently undertook a study to investigate the effectiveness of relatively inexpensive phosphabicyclononane[12] (Phoban) ligands as scaffolds for various catalytic metathesis reactions. Phoban ligand mixtures are currently used industrially for the cobalt-catalyzed hydroformylation reaction[13] and have found use for other catalytic processes.[14] 9-Cyclohexyl-9-phospha-9*H*-bicyclononane (**3**) was conveniently prepared as a ca. 3:1 mixture of [3.3.1]- and [4.2.1]-bridged isomers (**3a**,**b**) via radical addition of 1,5-cyclooctadiene to cyclohexylphosphine.[15] Alternatively, the isomerically pure [3.3.1] isomer **3a** was prepared by initial separation of isomeric

Scheme 1. Preparation of Cyclohexyl−phoban Derivatives 5 and 6



bicyclic secondary phosphabicyclononanes,[16] followed by treatment of the desired [3.3.1] isomer with *n*-butylithium and the phosphide thus formed was treated with bromocyclohexane. When **1** and **4**[17] were treated with a ca. 3:1 mixture of **3a**,**b**, ^{31}P NMR spectroscopy revealed that the symmetrical [3.3.1] isomer **3a** preferentially underwent ligand exchange reaction to afford exclusively **5**[18] and **6** in 72% and 75% yield, respectively (Scheme 1).[19] Alternatively, ligand exchange of **1** with isomerically pure **3a** provided **6** in 75% yield.[20] Formation of **5** and **6** can be monitored by ^{31}P NMR spectroscopy as the appearance of very broad singlets at δ 24.5 and 23.3 ppm, respectively.[21] The alkylidene proton (H_α) appears as a doublet ($^3J_{HH} = 11.52$ Hz) at δ 19.1 ppm for **5** and as a singlet at δ 20.2 ppm for **6**.

The isolated Ru−alkylidene complexes **5** and **6** are surprisingly air and moisture stable compared to **1** and can be stored in an ordinary vial for long periods. In solution **6** was stable in acetonitrile for at least 3 h, whereas decomposition was observed for complex **1** after only 3 min. Complex **5** remained unchanged after treatment with a 2 M HCl solution, while **1** instantly decomposed. Complex **6** is stable to column chromatography, can be recovered as a solid residue, and maintains its catalytic activity in subsequent metathesis reactions upon addition of new substrate (see below). In addition, complexes **5** and **6** display an improved thermal stability at elevated temperatures relative to **1**,[5a] allowing efficient metathesis reactions to be performed routinely above 50 °C.

The X-ray analysis[22] of **5** (Figure 1) indicated a distorted-square-pyramidal geometry about the metal center in which the carbene ligand occupies the apical

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(15) On the industrial scale phosphine (PH_3) is added to cycloocta-1,5-diene to give a mixture of isomeric [3.3.1]- and [4.2.1]-bridged 9-phospha-9*H*-bicyclononane secondary phoban phosphines, which are subsequently treated with an alkene to afford the desired mixture of tertiary phosphines.[12]

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(18) ^{31}P NMR (121 MHz, C_7D_8) analysis of the reaction mixture indicated quantitative conversion of **4** to **5**. The reduced yield is largely due to the partial solubility of **5** in hexanes mixtures.

(19) When isomerically pure **3b** was reacted with **4**, no identifiable products were recovered.

(20) Full details of these studies will be disclosed in due course.

(21) Extensive NMR studies indicate that **6** is resolved into a number of rotational isomers at low temperature. Full details of these studies will be disclosed in due course.

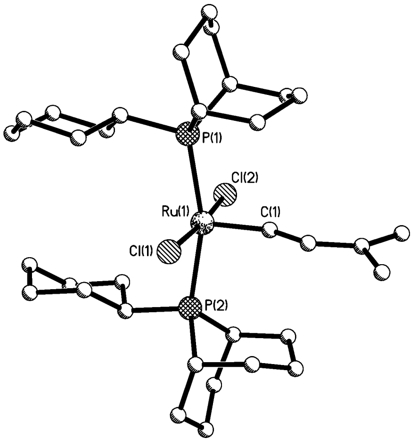

Figure 1. Perspective drawing of [$(PhobCy)_2Cl_2Ru{=}CHC{=}C(Me)_2$] (**5**).[22] The dimethylvinyl carbene system contained disorder at C(2), which was refined in two orientations (60/40 split), the higher occupancy orientation is illustrated.

Table 1. Metathesis Reactions via Ru−Alkylidene Catalysts

entry	substrate[a]	process	cat. (%)	conversn (%)[b]	selectivity (%)[b]	productive TON[c]
1	1-decene[d]	SM	**1** (0.01)	8	94	752
			2 (0.01)	52	63	3276
			6 (0.01)	77	98	7546
2	methyl oleate[d]	SM	**1** (0.0025)	7	95	2660
			2 (0.0025)	51	93	18972
			6 (0.0025)	47	97	18236
3	methyl oleate[e]	ethenolysis	**1** (0.003)	14	91	4247
			2 (0.003)	37	58	7153
			6 (0.003)	43	98	14047
4	diethyl diallyl malonate[f]	RCM	**1** (0.06)	59	95	934
			2 (0.06)	98	92	1502
			6 (0.06)	85	96	1360

[a] Purified by passing through alumina before use. [b] Determined by GC. [c] Productive TON = TON × (selectivity to required product). [d] Conditions: 60 °C, neat, 4 h. [e] Conditions: 10 bar of ethylene, 60 °C, neat, 2 h. [f] Conditions: 50 °C, 0.125 mM in toluene, 4 h.

position and the phosphine ligands in the basal plane occupy a trans position. The Ru−C1 bond distance (1.795(7) Å) is significantly shorter compared to the related Ph-substituted butylidene complex[2a] [$(PCy_3)_2Cl_2Ru{=}CHCH{=}CPh_2$] (**7**; 1.851(21) Å) and Cl-substituted benzylidene complex[2b] [$(PCy_3)_2Cl_2Ru{=}CH\text{-}p\text{-}C_6H_4\text{-}Cl$] (**8**; 1.839(3) Å). These data suggest a stronger Ru=C bond for **5** compared to that of other first-generation systems.

The isolated Ru alkylidene complexes are efficient catalysts for various metathesis reactions, particularly for applications where high selectivity is required. As depicted in Table 1, complex **6** is an efficient catalyst for self-metathesis (SM, entries 1 and 2), ethenolysis (entry 3), and RCM (entry 4) reactions. In all cases the catalytic activity of **6** is significantly greater than that of the first-generation catalyst **1**, while selectivity is maintained above 95%. Complex **6** is also an efficient catalyst for ring-opening metathesis polymerization (ROMP) reactions. For instance, ROMP of cyclooctadiene at 50 °C with 0.008 mol % of **6** gave 98% conversion to the corresponding polymer after 10 min, while under identical conditions 20% conversion was observed with **1**. Although complex **6** readily catalyzes the cross-metathesis (CM) of various functionalized olefins (Table 2), including 4° allylic carbon-containing olefins (entry 3), it shows no significant activity toward more difficult substrates such as acrylates and 1,1-disubstituted olefins.

Complex **6** can be recovered by column chromatography from metathesis reactions using concentrated catalyst solutions (>0.1 mol %) and used for subsequent metathesis reactions. For example, using **6** (2 mol %), the CM of styrene with 1-dodecene produced the cross-product in 87% conversion, and the catalyst was subsequently recovered and used for the self-metathesis of methyl oleate (46% conversion). Additional catalyst recovery by column chromatography provided further material that was used for the self-metathesis of 1-decene (70% conversion). When the present protocol is used, ^1H NMR indicates that the recovered catalyst is [$(PhobCy)_2Cl_2Ru{=}CHR$], where R is predominantly the alkylidene component(s) originating from the previous metathesis reaction.

Ruthenium methylidenes are key propagating species present within RCM, CM, and ethenolysis reactions and represent the thermally least stable intermediate species present within the catalytic metathesis cycle.[5a] Increasing understanding of the methylidene stability and decomposition pathways is critical for developing catalysts with extended lifetimes.[8] Thus, in an effort to gain a better insight into methylidene decomposition, the thermal decomposition of the deuterated carbene complex $(PhobCy)_2Cl_2Ru{=}CD_2$ (**9**) in benzene at 50 °C was studied by ^2H NMR. Under these conditions, after 20 min a sharp resonance at 5.25 ppm, corresponding to $D_2C{=}CD_2$, and a broad signal between δ 1.0 and 2.3 ppm, corresponding to saturated aliphatic resonances, were observed, along with the original carbene signal (δ 19.2 ppm).[23−25] Given that bimolecular decomposition products (ethylene) have not been observed previously for other bis-phosphine methylidene complexes,[5a] these observations suggest that the phosphabicyclononane ligand present within **9** is altering the relative rates of bimolecular and unimolecular decomposition pathways relative to those of other first-generation catalysts. Experimentally, these observations are evidenced by increased catalyst stability, particularly for ethenolysis reactions, in which the ruthenium methylidene is a key propagating species in the catalytic metathesis cycle. For example, ethenolysis of methyl oleate[6] using **6** allows reactions to be performed at higher temperatures relative to **1**, a natural consequence of which is higher activity and shorter reaction times.[27]

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(22) Crystal structure data for **5**: $C_{39}H_{64}Cl_2P_2Ru$, M_r = 766.81, orthorhombic, space group $P2_12_12_1$, a = 9.0223(14) Å. b = 9.8916(16) Å, c = 42.043(7) Å, V = 3752.1(10) Å^3, T = 125(2) K, Z = 4, ρ_{calcd} = 1.357 g cm^{-3}, SMART diffractometer, 19 470 reflections collected, 6761 unique reflections (R_{int} = 0.1270), R1 = 0.0520, wR2 = 0.0549, Flack parameter 0.01(4). The file CCDC-239497 contains supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB21EZ, U.K.; fax, (+44) 1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

(23) When the identical decomposition reaction was performed at 70 °C, no ethylene formation was observed.

(24) The methylidene complex $(PhobCy)_2Cl_2Ru{=}CH_2$ (**10**) decomposed with a half-life of 36 min at 70 °C. See the Supporting Information for more details.

(25) Grubbs et al. has reported that decomposition of the methylidene complex $(PCy_3)_2Cl_2Ru{=}CH_2$ (**11**) is primarily first order.[5a]

Table 2. Cross-Metathesis Reactions via Ru−Alkylidene Catalysts

entry	substrate[a]	cross-partner[a]	cat. (%)	con-versn (%)[b]	selec-tivity (%)[b]
1[c]	styrene	1-dodecene	**1** (0.25)	81	93
			2 (0.25)	87	41
			6 (0.25)	87	95
2[c]	styrene	5-hexene-2-one	**1** (0.50)	36	95
			2 (0.50)	99	90
			6 (0.50)	61	95
3[d]	4-hexen-1-yl acetate	3,3-dimethyl-1-butene	**1** (1.0)	0	−
			2 (1.0)	96	93
			6 (1.0)	53	96

[a] Purified by passing through alumina before use. [b] Determined by GC. [c] Conditions: substrate:cross-partner = 3:1, 50 °C, 4 h. [d] Conditions: excess cross-partner, 40 °C, 8 h.

In summary, the ruthenium carbene complexes **5** and **6** bearing phosphabicyclononane ligands are robust and recyclable catalysts for a variety of metathesis reactions. These complexes are more stable and active than the first-generation catalyst **1**, can be accessed from simple precursors,[17] and although they do not share the same broad application profile of second-generation catalysts, they are very useful in situations where high selectivity is required.[28] A full DFT comparison of complexes **5** and **6** with classical Grubbs carbenes **1** and **2**, along with NMR studies devoted to the study of rotational isomerization within cyclohexylphoban-containing Grubbs catalysts, will be reported shortly.

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Supporting Information Available: Text and tables giving experimental data for the synthesis of all new complexes, metathesis experiments, and crystallographic data (atomic coordinates, all bond distances and angles, and anisotropic displacement parameters) for complex **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[26] (a) Six, C.; Gabor, B.; Görls, H.; Mynott, R.; Philipps, P.; Leitner, W. *Organometallics* **1999**, *18*, 3316−3326. (b) Jafarpour, L.; Schanz, H.-J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 5416−5419 and references therein. (c) Amoroso, D.; Yap, G. P. A.; Fogg, D. E. *Can. J. Chem*. **2001**, *79*, 958−963.

[27] See the Supporting Information for more details.

[28] Forman, G. S.; McConnell, A. E.; Tooze, R. P.; Dwyer, C.; Serfontein, D. W. (Sasol Technology UK) World Patent ZA03/00087, 2003.