Olefin Oxygenation

DOI: 10.1002/anie.200705802

From Olefins to Ketones via a 2-Rhodaoxetane Complex**

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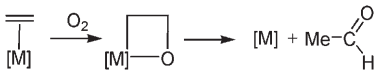
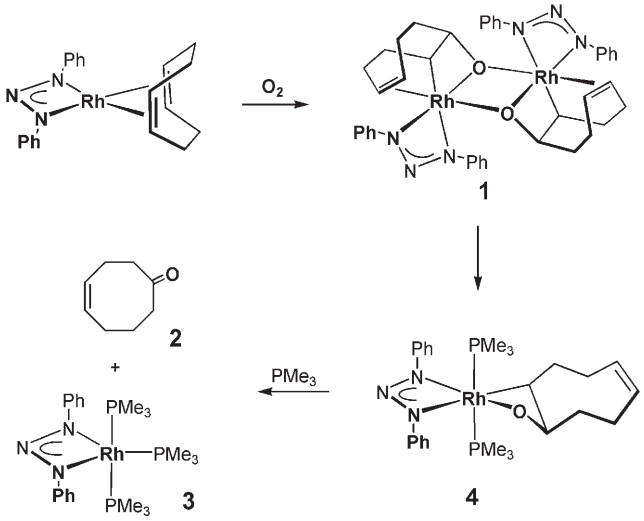
Oxidation reactions yielding valuable products from organic raw materials are one of the most problematic transformations although they constitute industrial core technologies. Moreover, the present main challenge and goal in oxidation is to perform these reactions with no waste and by using environmentally friendly oxidants such as oxygen[1] and hydrogen peroxide.[2] Significantly, epoxides, the typical product of the oxygenation of olefins catalyzed by complexes of the middle transition metals,[3] have rarely been evoked as products in rhodium chemistry. Oxidations using rhodium compounds are characterized by excellent selectivity for formation of methyl ketones from terminal olefins.[4] From the recently reviewed[4a] stoichiometric rhodium oxygenation reactions, it appears that rhodaoxetanes could be considered as viable intermediates in catalytic reactions. However, very few compounds with a 2-rhoda(III)oxetane ring have been reported to date. Moreover, the next step in a catalytic cycle to yield an oxygenated organic compound has a sole reported example, the formation of acetaldehyde and acetone from a 2-rhoda(III)oxetane derived from ethene or propene, respectively (Scheme 1).[5] The key reductive elimination step,



Scheme 1. Oxygenation and reductive elimination steps in the formation of carbonyl compounds from olefins.

fundamental for possible catalytic cycles in oxygenation of olefins, is poorly understood. Herein we address this reaction and report on the stoichiometric elimination of a ketone from a 2-rhoda(III)oxetane complex on addition of P-donor ligands.

We have previously described[6] facile oxygenation of $[Rh(PhN_3Ph)(C_8H_{12})]$ (C_8H_{12} = 1,5-cyclooctadiene = cod, PhN_3Ph = 1,3-diphenyltriazenide) with dioxygen to give dinuclear 2-rhoda(III)oxetane complex $[\{Rh(PhN_3Ph)(OC_8H_{12})\}_2]$ (**1**, Scheme 2), in which both oxygen atoms



Scheme 2. Characterized compounds in the stoichiometric oxygenation of cod to 4-cyclooctenone.

from dioxygen were incorporated with 100% atom efficiency. On treating a suspension of **1** with trimethylphosphane in $[D_6]$benzene at 35 °C, quantitative elimination of the organic fragment as 4-cyclooctenone (**2**) and formation of pentacoordinate Rh^I complex $[Rh(PhN_3Ph)(PMe_3)_3]$ (**3**) was observed (Scheme 2). This result provides new insight into the oxygenation of olefins with dioxygen, because it shows for the first time formation of a ketone from an isolated 2-rhoda(III)oxetane complex resulting from an internal olefin. Another interesting feature of the reductive elimination of 4-cyclooctenone from **1** is the absence of the phosphane oxide, typically produced in related reactions involving olefins, dioxygen, and phosphanes.[7]

The organic product 4-cyclooctenone was identified by GC-MS and NMR spectroscopy, while complex **3** was characterized by comparison of its spectroscopic data with those of pure samples prepared by alternative methods. Thus, **3** was straightforwardly prepared by reaction of $[Rh(PhN_3Ph)(C_8H_{12})]$ with PMe_3. The most relevant spectroscopic data of **3** are the two signals (in 2:1 ratio) corresponding to an AB_2X ($X = {}^{103}Rh$) pattern in the $^{31}P\{^1H\}$ NMR spectrum.

Monitoring the reaction of **1** with PMe_3 at 20 °C by NMR spectroscopy revealed that the coordination of two phosphane ligands occurs initially to give observable intermediate $[Rh(PhN_3Ph)(OC_8H_{12})(PMe_3)_2]$ (**4**). Complex **4** then undergoes reductive elimination to give 4-cyclooctenone spontaneously (see the Supporting Information). One additional molar equivalent of PMe_3 is required to recover the triazenerhodium(I) fragment as $[Rh(PhN_3Ph)(PMe_3)_3]$ (**3**); otherwise, formation of **3** is accompanied by formation of another unknown species.

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[**] The generous financial support from MEC/FEDER (Project CTQ2005-06807) and DGA (PIP 019/2005) is gratefully acknowledged. M.P.R. thanks DGA (Diputación General de Aragón) for a fellowship

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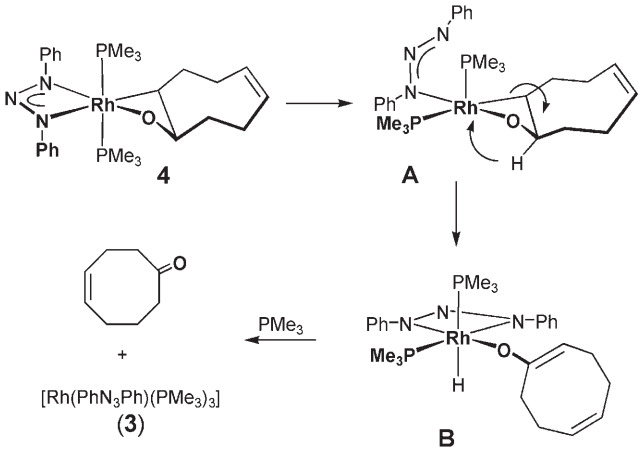
The *trans* disposition of the PMe_3 ligands in **4** was evident from the ABX pattern observed in the $^{31}P\{^1H\}$ NMR spectrum ($J_{P,P}$ = 493 Hz). The carbon atoms of the uncoordinated C=C double bond give rise to singlets at δ = 132.8 and 130.8 ppm in the $^{13}C\{^1H\}$ NMR spectrum. Finally, the presence of the 2-rhoda(III)oxetane moiety in **4** was deduced from the apt-$^{13}C\{^1H\}$ NMR spectrum, which showed signals for two HC groups at δ = 11.0 ($J_{C,Rh}$ = 17 Hz, CHRh) and 94.7 ppm ($^2J_{C,Rh}$ = 4 Hz, CHORh).

Once we identified key species **4**, we could propose a plausible mechanism leading to 4-cyclooctenone (Scheme 3).

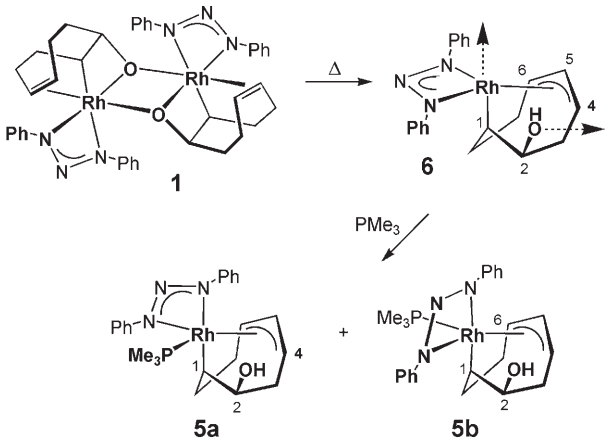


Scheme 3. Possible mechanism for ketone elimination from **4**.

The first step is bridge splitting of **1** and replacement of the coordinated C=C bond by a second equivalent of PMe_3 to form octahedral complex **4**. At this stage, the coordinative vacancy required for β-hydrogen elimination could be provided by hemilabile behavior of the triazenide ligand. Thus, the Rh–N bond *trans* to the alkyl group could be easily cleaved to give the 16-electron species **A**, which would undergo β-hydrogen elimination to give hydride enolate complex **B**. From **B**, reductive elimination accomplished by coordination of PMe_3 would give cycloocta-1,5-dien-1-ol and complex **3**, as observed. Note that the alternative direct reductive elimination from **4** to give the epoxide as product does not occur, and that ketone elimination requires the coordination of an additional ligand.

The role of temperature in the quantitative formation of 4-cyclooctenone is critical. At higher temperatures, the rate of the elimination reaction increases markedly, but the yield of the ketone decreases (66% at 65 °C for 1 h). Under these conditions the rhodium-containing products were a mixture of **3** (66%) and $[Rh(PhN_3Ph)(HOC_8H_{11})(PMe_3)]$ (**5**, 33%; Scheme 4). The latter was found to be the result of a side reaction involving isomerisation of **1** to the hydroxyallyl derivative **6** with coordination of trimethylphosphane.

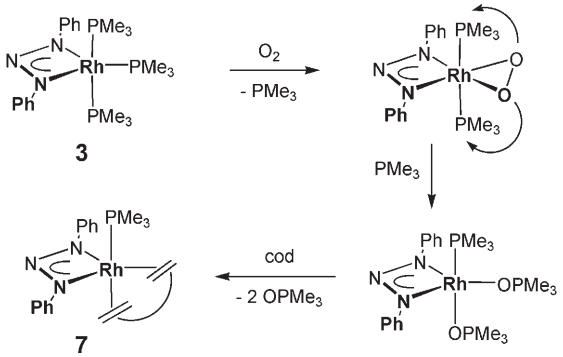
We previously observed[6] that **1** is kinetically unstable and forms $[\{Rh(PhN_3Ph)(HOC_8H_{11})\}_n]$ (**6**) on heating in $[D_6]$benzene at 65 °C. Accordingly, complex **5** results quantitatively from the reaction of **6** with PMe_3, as observed in a separate experiment. Complex **5** is inert towards reductive elimination reactions, and thus it is recovered unaltered even after heating in the presence of trimethylphosphane in toluene at 100 °C for 3 h.



Scheme 4. Reactions competing with ketone elimination.

Complex **5** was found to be a mixture of stereoisomers (**5a**/**5b** 3:1; Scheme 4), while the expected isomer having the PMe_3 ligand *trans* to C1 was not observed. Both isomers were easily identified in the $^1H,^1H$ NOESY spectrum, since the methyl groups from the PMe_3 ligands gave strong nOe cross-peaks only with protons H6 and H4, respectively (see the Supporting Information).

In order to close the hypothetical catalytic cycle, the reaction of $[Rh(PhN_3Ph)(PMe_3)_3]$ (**3**) with dioxygen was also investigated. On treatment of a solution of **3** in $[D_6]$benzene with neat O_2, complete transformation of all trimethylphosphane ligands into the oxide $OPMe_3$ was the only process identified. However, if the oxygenation reaction of **3** is carried out in the presence of 1,5-cyclooctadiene, clean transformation of **1** into $[Rh(PhN_3Ph)(cod)(PMe_3)]$ (**7**) and two molar equivalents of $OPMe_3$ occurs. The formation of **7** most probably involves the sequence of reactions shown in Scheme 5. It is reasonable to assume dissociation of one PMe_3 ligand in **3**, which is followed by oxidative addition of O_2 to give dioxygen complex **C**. In this complex, intramolecular oxygen transfer to the phosphorus atoms would give the phosphane oxide, which is easily replaced by free trimethylphosphane and cod to form **7**. Unfortunately, complex **7** does not react further with oxygen.



Scheme 5. Possible mechanism for the formation of **7**.

Previous work on olefin oxygenation reactions by rhodium complexes in the presence of phosphanes were systematically associated with formation of phosphane oxide, and from these observations the assumption that these processes require a sacrificial reducing agent to consume one oxygen atom was established. However, this study unequivocally shows that formation of 4-cyclooctenone and $OPMe_3$ are two independent processes, each of which involves one molecule of dioxygen and occurs with 100% atom efficiency. Moreover, 4-cyclooctenone is the sole elimination product from the isolated 2-rhoda(III)oxetane compound.

In conclusion, the present work clearly shows that rhodaoxetanes can be intermediates in the synthesis of carbonyl compounds from olefins in rhodium chemistry, and they are the origin of the excellent selectivity in the oxidation of olefins to ketones. This process also occurs with internal olefins, for which the reductive elimination step of a ketone from a 2-rhoda(III)oxetane compound on addition of a phosphane ligand has been documented here. Developing these stoichiometric reactions into catalytic process in the absence of phosphanes is a challenge for the future.

Experimental Section

3: Heating a red suspension of $[\{Rh(PhN_3Ph)(C_8H_{12})\}_2]$ (100.0 mg, 0.12 mmol) in toluene (5 mL) and PMe_3 (130.3 μL, 1.47 mmol) at 65 °C produced a red solution in 2 h. Concentration of this solution to ca. 3 mL and addition of pentane (8 mL) led to crystallization of the complex. The red solid was collected by filtration, washed with pentane (2 × 5 mL), and vacuum-dried. Yield: 106.8 mg (82%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.32 (dd, $^3J_{H,H}$ = 8.5 Hz, $^4J_{H,H}$ = 1.2 Hz, 4H; H^o), 7.42 (dd, $^3J_{H,H}$ = 8.5, 7.3 Hz, 4H; H^m), 7.09 (tt, $^3J_{H,H}$ = 7.3 Hz, $^4J_{H,H}$ = 1.2 Hz, 2H; H^p), 1.12 (m, 9H; CH_3), 1.07 ppm (m, 18H; CH_3); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 °C): δ = −6.6 (dt, $J_{P,Rh}$ = 155 Hz, $^2J_{P,P}$ = 47 Hz, 1P), −15.3 (dd, $J_{P,Rh}$ = 137, $^2J_{P,P}$ = 47 Hz, 2P); C,H,N analysis calcd (%) for $C_{21}H_{37}N_3P_3Rh$: C 47.83, H 7.07, N 7.97; found: C 47.79, H 7.38, N 7.61.

4: Neat PMe_3 (10.5 μL, 0.12 mmol) was added to a suspension of $[\{Rh(PhN_3Ph)(OC_8H_{12})\}_2]$ (**1**, 16.1 mg, 0.02 mmol) in [D$_6$]benzene (0.5 mL) and the reaction was monitored by NMR spectroscopy. After 6 h at 20 °C the main complex was found to be **4**. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C, TMS): δ = 7.57 (d, $^3J_{H,H}$ = 7.5 Hz, 2H; H$^{o'}$), 7.38 (d, $^3J_{H,H}$ = 7.5 Hz, 2H, H$^{o''}$), 7.23 (t, $^3J_{H,H}$ = 7.5 Hz, 2H; H$^{m'}$), 7.17 (t, $^3J_{H,H}$ = 7.5 Hz, 2H; H$^{m''}$), 6.91 (t, $^3J_{H,H}$ = 7.3 Hz, 1H; H$^{p'}$), 6.90 (t, $^3J_{H,H}$ = 7.3 Hz, 1H; H$^{p''}$), 5.95 (m, 1H; H5), 5.84 (m, 1H; H6), 4.85 (m, 1H; H2), 2.69 (m, 1H; H1), 2.54 (m, 1H; H7a), 2.37 (m, 1H; H8a), 2.19 (m, 1H; H7b), 2.09 (m, 1H; H4a), 2.04 (m, 1H; H8b), 1.96 (m, 1H; H3a), 1.94 (m, 1H; H4b), 1.80 (m, 1H; H3b), 1.13 (d, $^2J_{H,P}$ = 6.6 Hz, 9H), 1.11 ppm (d, $^2J_{H,P}$ = 6.3 Hz, 9H; PMe_3); ^{31}P{^{1}H} NMR (121 MHz, [D$_6$]benzene, 25 °C): δ = −8.76 (δ_A, $J_{P,Rh}$ = 116 Hz), −11.8 ppm (δ_B, $J_{P,Rh}$ = 120 Hz, $^2J_{A,B}$ = 493 Hz); ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25 °C, TMS): δ = 150.5 (C$^{i'}$), 150.3 (d, $^2J_{C,Rh}$ = 3 Hz; C$^{i''}$), 132.8 (C5), 130.8 (C6), 129.5 (C$^{m'}$), 129.1 (C$^{m''}$), 123.6 (C$^{p'}$), 123.4 (C$^{p''}$), 117.9 (C$^{o'}$), 117.2 (C$^{o''}$), 94.7 (d, $^2J_{C,Rh}$ = 4 Hz; C2), 40.5 (C3), 38.7 (m, C8), 28.8 (t, $^4J_{C,P}$ = 3 Hz; C7), 22.4 (C4), 15.3 and 13.4 (2 × vq; PMe_3), 11.0 ppm (dt, $J_{C,Rh}$ = 17 Hz, $^2J_{C,P}$ = 3 Hz; C1).

5: Complex **1** was fully transformed into isomeric hydroxyallyl complex **6** by heating a suspension of **1** (130.0 mg, 0.15 mmol) in toluene (15 mL) for 1 h 30 min at 100 °C. Further addition of PMe_3 (27 μL, 0.31 mmol) immediately gave a dark green solution, which was filtered over kieselguhr, concentrated to ca. 2 mL, and carefully layered with pentane (8 mL) to give green microcrystals of **5** overnight. The solution was decanted and the solid washed with cold pentane (2 × 5 mL) and vacuum-dried. Yield: 90.5 mg (60%). C,H,N analysis calcd (%) for $C_{23}H_{31}N_3PORh$: C 55.32, H 6.26, N 8.41; found: C 55.43, H 6.16, N 8.57; ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C, TMS): **5a**: δ = 7.62 (d, $^3J_{H,H}$ = 7.8 Hz, 2H; H$^{o'}$), 7.301 (t, $^3J_{H,H}$ = 7.8 Hz, 2H; H$^{m'}$), 7.21 (t, $^3J_{H,H}$ = 7.8 Hz, 2H; H$^{m''}$), 7.15 (2H; H$^{o''}$), 7.00 (m, 1H; H$^{p'}$), 6.93 (t, $^3J_{H,H}$ = 8.0 Hz, 1H; H$^{p''}$), 5.53 (m, 1H; H6), 4.81 (t, $^3J_{H,H}$ = 8.1 Hz, 1H; H5), 3.92 (m, 1H; H4), 3.06 (br d, $^3J_{H,H}$ = 4.1 Hz, 1H; H2), 2.59 (vt, 1H; H1), 2.32 (m, 1H; H8′), 1.59 (m, 1H; H7′), 1.53 (m, 2H; H3′ + H3″), 1.23 (d, $^2J_{H,P}$ = 9.7 Hz, 9H; PMe_3), 1.18 (m, 1H; H8″), 0.95 (m, 1H; H7″), 0.81 (d, $^3J_{H,H}$ = 12.9 Hz, 1H; OH); **5b**: δ = 7.82 (d, $^3J_{H,H}$ = 8.0 Hz, 2H; H$^{o'}$), 7.305 (m, $^3J_{H,H}$ = 8.0 Hz, 2H; H$^{m'}$), 7.20 (t, $^3J_{H,H}$ = 8.0 Hz, 2H; H$^{m''}$), 7.05 (d, $^3J_{H,H}$ = 8.0 Hz, 2H; H$^{o''}$), 6.98 (m, 1H; H$^{p'}$), 6.91 (t, $^3J_{H,H}$ = 8.0 Hz, 1H; H$^{p''}$), 5.46 (m, 1H; H4), 4.76 (t, $^3J_{H,H}$ = 8.1 Hz, 1H; H5), 3.85 (m, 1H; H6), 3.46 (br d, $^3J_{H,H}$ = 12.0 Hz, 1H; H2), 2.98 (d, $^3J_{H,H}$ = 12.1 Hz, 1H; OH), 2.68 (vt, 1H; H1), 1.90 (m, 1H; H3′), 1.58 (m, 1H; H7′), 1.56 (m, 1H; H8′), 1.33 (m, 1H; H3″), 1.27 (m, 1H; H7″), 0.97 (m, 1H; H8″), 0.88 ppm (d, $^2J_{H,P}$ = 9.3 Hz, 9H; PMe_3). ^{31}P{^{1}H} NMR (121 MHz, [D$_6$]benzene, 25 °C): **5a**: δ = −5.9 ppm (d, $J_{P,Rh}$ = 164 Hz); **5b**: δ = 6.6 (d, $J_{P,Rh}$ = 163 Hz). ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25 °C, TMS): **5a**: δ = 155.6 (C$^{i'+i''}$), 129.5 (C$^{m''}$), 129.2 (C$^{m'}$), 123.0 (C$^{p'}$), 123.0 (C$^{p''}$), 117.9 (C$^{o'}$), 116.9 (C$^{o''}$), 101.7 (dd, $J_{C,Rh}$ = 4.1 Hz, $^2J_{C,P}$ = 2.0 Hz; C5), 90.4 (dd, $J_{C,Rh}$ = 30 Hz, $^2J_{C,P}$ = 5 Hz; C6), 89.3 (d, $^3J_{C,P}$ = 2.0 Hz; C2), 60.3 (d, $J_{C,Rh}$ = 12.6 Hz; C4), 49.9 (dd, $J_{C,Rh}$ = 21.7 Hz, $^2J_{C,P}$ = 6.5 Hz; C1), 44.2 (dd, $^3J_{C,P}$ = 10.3 Hz, $^2J_{C,Rh}$ = 1.4 Hz; C8), 37.9 (C3), 22.3 (d, $^3J_{C,P}$ = 4.1 Hz; C7), 17.5 ppm (dd, $J_{C,P}$ = 27.4 Hz, $^2J_{C,Rh}$ = 1.2 Hz; PMe_3); **5b**: δ = 152.2 (C$^{i'}$), 149.7 (C$^{i''}$), 129.5 (C$^{m'}$), 129.1 (C$^{m''}$), 123.6 (C$^{p'}$), 123.4 (C$^{p''}$), 119.1 (C$^{o'}$), 117.0 (C$^{o''}$), 101.2 (dd, $J_{C,Rh}$ = 4.1 Hz, $^2J_{C,P}$ = 2.4 Hz; C5), 90.3 (d, $^3J_{C,P}$ = 8.4 Hz; C2), 86.6 (dd, $J_{C,Rh}$ = 29.7 Hz, $^2J_{C,P}$ = 5.1 Hz; C4), 63.9 (d, $J_{C,Rh}$ = 12.9 Hz; C6), 49.7 (dd, $J_{C,Rh}$ = 21.3 Hz, $^2J_{C,P}$ = 5.7 Hz; C1), 40.5 (d, $^3J_{C,P}$ = 5.1 Hz; C8), 33.4 (d, $^3J_{C,P}$ = 4.0 Hz; C3), 24.6 (C7), 16.3 ppm (dd, $J_{C,P}$ = 27.0 Hz, $^2J_{C,Rh}$ = 1.2 Hz; PMe_3).

7: A suspension of $[\{Rh(PhNNNPh)(C_8H_{12})\}_2]$ (100.0 mg, 0.12 mmol) in toluene (5 mL) was heated for 5 min at 80 °C to achieve full dissolution of the complex. Then neat PMe_3 (21.7 μL, 0.25 mmol) was added dropwise to give an orange solution, which was evaporated to dryness. The residue was dissolved in pentane and the extract filtered over kieselguhr. The filtrate was concentrated to 3 mL and left overnight at −30 °C to afford orange crystals, which were separated by decantation and vacuum-dried. Yield: 88.1 mg (74.1%). ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C, TMS): δ = 7.82 (d, $^3J_{H,H}$ = 8.4 Hz, 4H; H^o), 7.32 (t, $^3J_{H,H}$ = 7.8 Hz, 4H; H^m), 6.97 (t, $^3J_{H,H}$ = 7.3 Hz, 2H; H^p), 3.85(br, 4H; HC=), 2.34 (m, 4H; CH_2), 1.86 (m, 4H; CH_2), 0.65 ppm (d, $^2J_{H,P}$ = 9.3 Hz, 9H; PMe_3); ^{31}P{^{1}H} NMR (121 MHz, [D$_6$]benzene, 25 °C): δ = −6.59 ppm (d, $J_{P,Rh}$ = 141.5 Hz; PMe_3); ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25 °C, TMS): δ = 151.2 (C^i), 129.3 (C^m), 122.5 (C^p), 118.2 (C^o), 80.2 (d, $J_{C,Rh}$ = 12.5 Hz; HC=), 32.2 (CH_2), 14.3 ppm (dd, $J_{C,P}$ = 28.9 Hz, $J_{C,Rh}$ = 0.95 Hz; PMe_3); C,H,N analysis calcd (%) for $C_{23}H_{31}N_3PRh$: C 57.15, H 6.46, N 8.69; found: C 57.21, H 6.35, N 8.89.

Received: December 12, 2007
Published online: February 22, 2008

Keywords: ketones · oxetanes · oxidation · oxygenation · rhodium

[1] See, for example: a) C. N. Cornell, M. S. Sigman, *Inorg. Chem.* **2007**, *46*, 1903–1909; b) M. G. Speziali, P. A. Robles-Dutenhefner, E. V. Gusevskaya, *Organometallics* **2007**, *26*, 4003–4009; c) K. M. Gligorich, M. S. Sigman, *Angew. Chem.* **2006**, *118*, 6764–6767; *Angew. Chem. Int. Ed.* **2006**, *45*, 6612–6615; d) J. Piera, K. Närhi, J.-E. Bäckvall, *Angew. Chem.* **2006**, *118*, 7068–7071; *Angew. Chem. Int. Ed.* **2006**, *45*, 6914–6917; e) K. Ohkubo, T. Nanjo, S. Fukuzumi, *Catal. Today* **2006**, *117*, 356–361; f) D. G. H.

Hetterscheid, B. de Bruin, *J. Mol. Catal. A* **2006**, *251*, 291 – 296; g) *Catalysis by Metal Complexes*, *Vol. 26: Advances in Catalytic Activation of Dioxygen by Metal Complexes* (Ed.: L. I. Simándi), Kluwer Academic Publisher, Dordrecht, **2003**.

[2] See, for example: a) Y. Sawada, K. Matsumoto, T. Katsuki, *Angew. Chem.* **2007**, *119*, 4643 – 4645; *Angew. Chem. Int. Ed.* **2007**, *46*, 4559 – 4561; b) M. Colladon, A. Scarso, P. Sgarbossa, R. A. Michelin, G. Strukul, *J. Am. Chem. Soc.* **2007**, *129*, 7680 – 7689; c) I. W. C. E. Arends, *Angew. Chem.* **2006**, *118*, 6398 – 6400; *Angew. Chem. Int. Ed.* **2006**, *45*, 6250 – 6252.

[3] a) T. Punniyamurthy, S. Subbarayan, J. Iqbal, *Chem. Rev.* **2005**, *105*, 2329 – 2363; b) D. V. Deubel, G. Frenking, P. Gisdakis, W. A. Herrmann, N. Rösch, J. Sundermeyer, *Acc. Chem. Res.* **2004**, *37*, 645 – 652; c) *Modern Oxidation Methods* (Ed.: J.-E. Bäckvall), Wiley-VCH, Weinheim, **2004**.

[4] a) C. Tejel, M. A. Ciriano, *Top. Organomet. Chem.* **2007**, *22*, 97 – 124; b) B. de Bruin, P. H. M. Budzelaar, A. W. Gal, *Angew. Chem.* **2004**, *116*, 4236 – 4251; *Angew. Chem. Int. Ed.* **2004**, *43*, 4142 – 4157.

[5] a) B. de Bruin, J. A. W. Verhagen, C. H. J. Schouten, A. W. Gal, D. Feichtinger, D. A. Plattner, *Chem. Eur. J.* **2001**, *7*, 416 – 422; b) B. De Bruin, M. J. Boerakker, J. A. W. Verhagen, R. De Gelder, J. M. M. Smits, A. W. Gal, *Chem. Eur. J.* **2000**, *6*, 298 – 312.

[6] C. Tejel, M. A. Ciriano, E. Sola, M. P. del Río, G. Ríos-Moreno, F. J. Lahoz, L. A. Oro, *Angew. Chem.* **2005**, *117*, 3331 – 3335; *Angew. Chem. Int. Ed.* **2005**, *44*, 3267 – 3271.

[7] G. Read, *J. Mol. Catal.* **1991**, *64*, 15 – 33.

