of the PEA layer is assumed to be 0.5 μm, the ohmic resistance through the PPY wire within this coating is 100 Ω, and the actual potential on the PPY wire emerging from PEA film may be too small for oxidation of the monomer.

Our observations in this study are completely different from the template synthesis of nanowires by electropolymerization in nanoporous membranes.[6] In template synthesis, PPY begins to grow from the electrode surface, that is, from the foot of the pores. Then the growing PPY follows the pore wall and forms tubules, which as soon as they come out of the pores, grow as a continuous top layer. This growth mechanism is possible because the conductivity of PPY synthesized in water is sufficiently high. Moreover, the membrane is insoluble in the reaction medium, so that the monomer cannot diffuse through it to reach the electrode surface. It can only penetrate into the pores until they become completely blocked. This mechanism is thus fundamentally different from that observed in this work.

From the SEM images, the PPY wire has a diameter of approximately 600 nm and a length of about 300 μm. All the wires have an annular structure, which might be an imprint of the PEA channel through which the PPY grows. Figure 6 shows a set of wires that have grown from the electrode surface. The PPY wires are randomly dispersed on the whole electrode surface and have diameters between 400 nm and 1 μm.

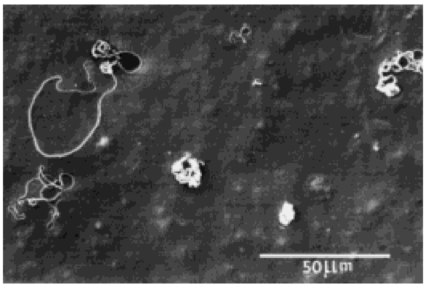


Figure 6. SEM image of PPY wires on PEA-grafted carbon.

According to the proposed PPY growth mechanism, there would be no intrinsic limit to the wire length; only the polarization time would be a limiting factor. As long as the formation of channels through the PEA film remains unexplained, the wire diameter and the density of the wires on the electrode surface cannot be predicted. Wire formation is actually controlled by the complex interaction of several parameters, including PPY conductivity, current density, PPY and Py diffusion rate through the swollen layer of grafted polymer, and hence the nature, thickness, and grafting density of the insulating polymer chains.

Experimental Section

Monomers, solvent, and conducting salt were dried before use. Electrochemical experiments were carried out in a one-compartment cell with a platinum pseudoreference electrode and a platinum counterelectrode with a PAR potentiostat (EG&G, Model 273 A) in a glovebox under a dry inert atmosphere. This technique is detailed elsewhere.[8, 9]

Received: March 19, 1998
Revised version: June 12, 1998 [Z11608IE]
German version: *Angew. Chem.* **1998**, *110*, 2639–2642

Keywords: conducting materials · electrochemistry · nanostructures · polymers

[1] G. A. Ozin, *Adv. Mater.* **1992**, *4*, 612.
[2] M. G. Kanatzidis, L. M. Tonge, T. J. Marks, H. O. Marcy, C. R. Kannewurf, *J. Am. Chem. Soc.* **1987**, *109*, 3797; M. G. Kanatzidis, C. G. Wu, H. O. Marcy, C. R. Kannewurf, *J. Am. Chem. Soc.* **1989**, *111*, 4139.
[3] T. Bein, P. Enzel, F. Beuneu, L. Zuppiroli, *Adv. Chem. Ser.* **1990**, *226*, 433.
[4] C. R. Martin, *Acc. Chem. Res.* **1995**, *28*, 61.
[5] Z. Cai, C. R. Martin, *J. Am. Chem. Soc.* **1989**, *111*, 4138.
[6] S. Demoustier-Champagne, E. Ferain, R. Legras, C. Jérôme, R. Jérôme, *Eur. Polym. J.*, in press.
[7] R. V. Parthasarathy, C. R. Martin, *Chem. Mater.* **1994**, *6*, 1627.
[8] R. Jérôme, M. Mertens, L. Martinot, *Adv. Mater.* **1995**, *7*, 807.
[9] N. Baute, P. Dubois, L. Martinot, M. Mertens, P. Teyssié, R. Jérôme, *Eur. J. Inorg. Chem.*, submitted.
[10] C. P. Andrieux, P. Audebert, P. Hapiot, J. M. Savéant, *J. Phys. Chem.* **1991**, *95*, 10158.
[11] S. Asavapiriyanont, G. K. Chandler, G. A. Gunawardena, D. Pletcher, *J. Electroanal. Chem.* **1984**, *177*, 229.
[12] J. Ouyang, Y. Li, *Polymer* **1997**, *38*, 1971.

A Novel Class of Ruthenium Catalysts for Olefin Metathesis**

Thomas Weskamp, Wolfgang C. Schattenmann,
Michael Spiegler, and Wolfgang A. Herrmann*

*Dedicated to Professor Heinrich Nöth
on the occasion of his 70th birthday*

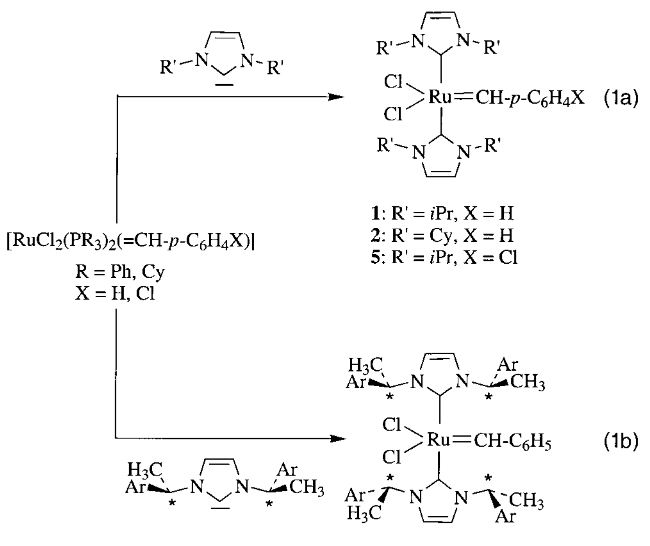
Transition metal catalyzed C–C bond formation is a focal issue in both organic synthesis and polymer chemistry.[1] One of these C–C coupling processes is olefin metathesis encompassing reactions such as ring-opening metathesis polymerization (ROMP), acyclic diene metathesis reaction (ADMET), ring-closing metathesis (RCM), and metathesis of acyclic olefins.[2] In this area ruthenium–phosphane complexes have conveyed much progress,[3] since they tolerate polar functional groups. Herein, we report the first ruthenium-based examples of a new class of compounds containing alkylidene groups as well as N-heterocyclic carbenes[4–6] as ligands and their application as catalysts in olefin metathesis.

The phosphane complex [$RuCl_2(PPh_3)_2(=CHPh)$] developed by Grubbs et al.[3d] reacts with 2.2 equivalents of the appropriate imidazolin-2-ylidene to yield compounds **1**–**4**

---

[*] Prof. Dr. W. A. Herrmann, Dipl.-Chem. T. Weskamp,
Dr. W. C. Schattenmann, Dipl.-Chem. M. Spiegler
Anorganisch-chemisches Institut
der Technischen Universität München
Lichtenbergstrasse 4, D-85747 Garching (Germany)
Fax: (+49) 89-289-13473
E-mail: lit@arthur.anorg.chemie.tu-muenchen.de

[**] This work was supported by the Fonds der Chemischen Industrie (Ph.D. fellowship to T. W.), the Bayerische Forschungsstiftung (Bayerischer Forschungsverbund Katalyse, FORKAT), the Deutsche Forschungsgemeinschaft, and Degussa AG (loans of $RuCl_3$).



1: R' = *i*Pr, X = H
2: R' = Cy, X = H
5: R' = *i*Pr, X = Cl

***(R,R)*-3**: Ar = Ph
***(R,R)*-4**: Ar = Naph

(Cy = cyclohexyl, Naph = 1-naphthyl) as air-stable solids in 80–90 % yield [Eq. (1 a, b)].[7] The given complexes can also be prepared in high yields from [RuCl$_2$(PCy$_3$)$_2$(=CHPh)], thus demonstrating the stronger Lewis basicity of N-heterocyclic carbenes as compared to that of trialkylphosphanes. Compounds (*R,R*)-**3** and (*R,R*)-**4** are promising extensions of the established ruthenium-based metathesis catalysts as they exhibit *chiral* imidazolin-2-ylidene ligands. A single-crystal X-ray analysis of **5** (Figure 1)[8] reveals a lower degree of distortion of the square-pyramidal coordination than the analogous phosphane complex [RuCl$_2$(PCy$_3$)$_2$(=CH-p-C$_6$H$_4$Cl)].[3d,10] The Ru–C bond lengths of the alkylidene (1.821(3) Å) and the *N*-heterocyclic carbene (2.107(3), 2.115(3) Å) moieties, mirror the fundamentally different nature of metal–"carbene" bonds ($\Delta d \approx 0.3$ Å).

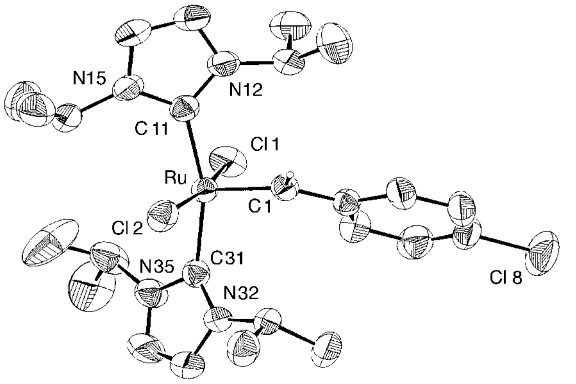


Figure 1. Platon[9] plot of **5**. Thermal ellipsoids are at 50 % probability. All H atoms except at C1 are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru–Cl1 2.3995(9), Ru–Cl2 2.3921(8), Ru–C1 1.821(3), Ru–C11 2.107(3), Ru–C31 2.115(3); Cl1-Ru-Cl2 170.32(3), Cl1-Ru-C1 98.37(10), Cl1-Ru-C11 88.26(8), Cl1-Ru-C31 94.76(8), Cl2-Ru-C1 91.14(10), Cl2-Ru-C11 89.21(8), Cl2-Ru-C31 85.14(8), C1-Ru-C11 94.48(12), C1-Ru-C31 100.92(13), C11-Ru-C31 163.68(11).

Our new compounds show unexpected behavior in solution as demonstrated by their ^{1}H and ^{13}C NMR spectra (Table 1).

Table 1. Selected NMR-spectroscopic data for compunds **1**–**5**.

1: ^{1}H NMR (CD$_2$Cl$_2$, 200 K): $\delta = 20.33$ (1H, s, Ru=CH), 7.15 (2H, br, NCH), 7.03 (2H, br, NCH), 5.97 (2H, m, $^3J_{HH} = 6.4$ Hz, NC*H*Me$_2$), 3.73 (2H, m, $^3J_{HH} = 6.4$ Hz, NC*H*Me$_2$), 1.64 (12H, d, $^3J_{HH} = 6.4$ Hz, NCH*Me*$_2$), 1.11 (6H, d, $^3J_{HH} = 6.4$ Hz, NCH*Me*$_2$), 0.75 (6H, d, $^3J_{HH} = 6.4$ Hz, NCH*Me*$_2$); ^{13}C NMR (CD$_2$Cl$_2$, 200 K): $\delta = 295.6$ (Ru=CH), 183.5 (NCN), 118.1 and 117.2 (NCH), 52.1 and 50.1 (N*C*HMe$_2$), 24.5, 23.8, 23.8 and 22.4 (NCH*Me*$_2$), ^{1}H NMR (CD$_2$Cl$_2$, 298 K): $\delta = 20.45$ (1H, s, Ru=CH), 7.14 (2H, br, NCH), 7.00 (2H, br, NCH), 6.06 (2H, br, NC*H*Me$_2$), 3.82 (2H, br, NC*H*Me$_2$), 1.64 (12H, br, NCH*Me*$_2$), 0.93 (12H, br, NCH*Me*$_2$); ^{13}C NMR (CD$_2$Cl$_2$, 298 K): $\delta = 295.6$ (Ru=CH), 183.5 (NCN), 118.3 and 117.5 (br, NCH), 52.5 and 50.5 (br, N*C*HMe$_2$), 24.1 (br, NCH*Me*$_2$)

2: ^{1}H NMR (CD$_2$Cl$_2$, 298 K): $\delta = 20.45$ (1H, s, Ru=CH), 7.14 (2H, br, NCH), 7.00 (2H, br, NCH), 6.06 (2H, br, CH of NC$_6$H$_{11}$), 3.82 (2H, br, CH of NC$_6$H$_{11}$), 1.64 (12H, br, CH$_2$ of NC$_6$H$_{11}$), 0.93 (12H, br, CH$_2$ of NC$_6$H$_{11}$); ^{13}C NMR (CD$_2$Cl$_2$, 298 K): $\delta = 299.4$ (Ru=CH), 182.9 (NCN), 118.3 and 117.8 (br, NCH), 59.6 and 57.5 (br, CH of NC$_6$H$_{11}$), 35.7, 26.9 and 25.6 (br, CH$_2$ of NC$_6$H$_{11}$)

(*R,R*)-**3**: ^{1}H NMR (CD$_2$Cl$_2$, 200 K): $\delta = 20.26$ (1H, s, Ru=CH), 4.91 (2H, m, NC*H*MePh), 1.84 (3H, d, $^3J_{HH} = 6.6$ Hz, NCH*Me*Ph), 1.81 (3H, d, $^3J_{HH} = 6.6$ Hz, NCH*Me*Ph), 1.51 (3H, d, $^3J_{HH} = 6.6$ Hz, NCH*Me*Ph), 1.21 (3H, d, $^3J_{HH} = 6.6$ Hz, NCH*Me*Ph); ^{13}C NMR (CD$_2$Cl$_2$, 200 K): $\delta = 294.7$ (Ru=CH), 186.0 and 185.6 (NCN), 141.2, 140.3, 140.1 and 139.9 (*ipso*-C of NCHMe*Ph*), 120.5, 119.9, 119.2 and 118.8 (NCH), 57.6, 57.4, 56.7 and 56.1 (N*C*HMePh), 22.2, 20.6, 20.4 and 20.3 (NCH*Me*Ph); ^{1}H NMR (CD$_2$Cl$_2$, 298 K): $\delta = 20.43$ (1H, s, Ru=CH), 5.09 (2H, br, NC*H*MePh), 2.02–1.20 (12H, br, NCH*Me*Ph); ^{13}C NMR (CD$_2$Cl$_2$, 298 K): $\delta = 294.8$ (Ru=CH), NCN not detected, *ipso*-C of NCHMe*Ph* not detected, 120.5 and 119.5 (br, NCH), 58.3 and 57.3 (br, N*C*HMePh), 21.5 (br, NCH*Me*Ph)

(*R,R*)-**4**: ^{1}H NMR (CD$_2$Cl$_2$, 260 K): $\delta = 20.90$ (1H, s, Ru=CH); ^{13}C NMR (CD$_2$Cl$_2$, 260 K): $\delta = 299.9$ (Ru=CH), 187.2 and 184.7 (NCN), 121.7, 121.0, 119.9 and 118.9 (NCH), 56.7, 56.1, 55.0 and 54.7 (N*C*HMeNaph), 24.7, 24.3, 21.0 and 20.0 (NCH*Me*Naph)

5: ^{1}H NMR (CD$_2$Cl$_2$, 200 K): $\delta = 20.33$ (1H, s, Ru=CH), 7.15 (2H, br, NCH), 7.03 (2H, br, NCH), 5.97 (2H, m, $^3J_{HH} = 6.4$ Hz, NC*H*Me$_2$), 3.73 (2H, m, $^3J_{HH} = 6.4$ Hz, NC*H*Me$_2$), 1.64 (12H, d, $^3J_{HH} = 6.4$ Hz, NCH*Me*$_2$), 1.11 (6H, d, $^3J_{HH} = 6.4$ Hz, NCH*Me*$_2$), 0.75 (6H, d, $^3J_{HH} = 6.4$ Hz, NCH*Me*$_2$); ^{13}C NMR (CD$_2$Cl$_2$, 200 K): $\delta = 295.6$ (Ru=CH), 183.5 (NCN), 118.1 and 117.2 (NCH), 52.1 and 50.1 (N*C*HMe$_2$), 24.5, 23.8, 23.8 and 22.4 (NCH*Me*$_2$)

The alkylidene moiety—usually written as a "double bond" (σ donor/π acceptor)—freely rotates around the Ru–C bond at room temperature. In contrast, the spectra reveal hindered rotation of the Ru–C linkage of the N-heterocyclic carbene ligands—usually written as a "single bond" (σ donor, virtually no π acceptor). Steric hindrance is the only reasonable explanation for this phenomenon.

Complexes **1**–**4** are remarkably active catalysts in ROMP and RCM; the results of selected ROMP experiments are shown in Figure 2 and Table 2. A striking feature of the catalytic cyclooctene polymerization is the pronounced dependence on the *N*-heterocyclic carbene ligand. While **1** ($M_n = 266$ kg mol^{-1}; PDI (polydispersity index): 1.76; 86 % *trans*) and **2** ($M_n = 205$ kg mol^{-1}; PDI: 1.71; 78 % *trans*) give polymers in near quantitative yields within one hour at room temperature, virtually no polymer is obtained under the same conditions using (*R,R*)-**3**, and only a modest yield with (*R,R*)-**4**. At elevated temperatures, however, (*R,R*)-**3** and (*R,R*)-**4** unfold higher catalytic activities. This indicates that subtle steric effects can be exploited to tune the catalytic performance much better than with phosphane ligands. The new

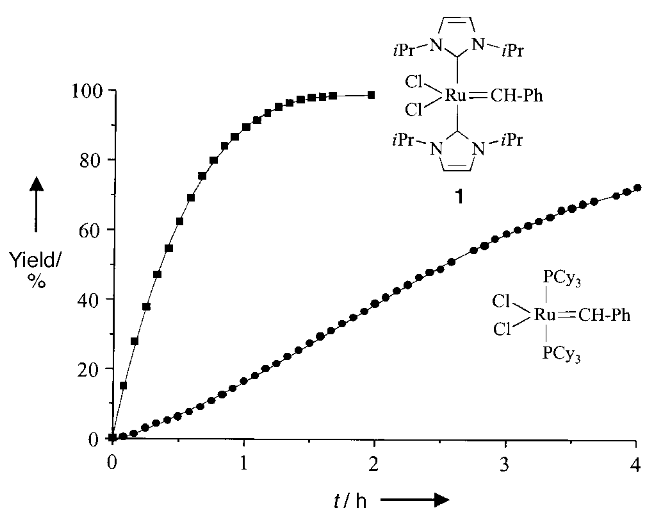


Figure 2. ROMP of cyclooctene. NMR-monitored comparison of **1** and a known ruthenium phosphane catalyst.[3d, 10] $T = 25\,^{\circ}\mathrm{C}$, 2.50 µmol catalyst in 0.50 mL of CD_2Cl_2; [cyclooctene]/[catalyst] = 250/1.

Table 2. ROMP of 2-norbornene and cyclooctene.[a]

Catalyst	Olefin	T [°C]	t [min]	Yield [%]
1	2-norbornene[b]	25	1	91
2	2-norbornene[b]	25	1	92
1	cyclooctene[c]	25	60	84
1	cyclooctene[c]	25	120	97
2	cyclooctene[c]	25	60	87
(*R,R*)-**3**	cyclooctene[c]	25	60	3
(*R,R*)-**3**	cyclooctene[c]	60	60	72
(*R,R*)-**4**	cyclooctene[c]	25	60	54
(*R,R*)-**4**	cyclooctene[c]	60	60	89

[a] Reactions at 25 °C: Catalyst (6.30 µmol) in CH_2Cl_2 (0.50 mL); at 60 °C: Catalyst (6.30 µmol) in $ClCH_2CH_2Cl$ (0.50 mL); [b] [norbornene]/[catalyst] = 100/1; [c] [cyclooctene]/[catalyst] = 500/1.

catalysts also show high resistance towards functional groups. Derivatives of norbornene with a variety of polar functionalities (e.g., aldehyde, alcohol, ketone, carboxylic acid, carboxylic ester) are readily polymerized with **1**.[11]

Recently, a great deal of interest has been devoted to RCM in the total synthesis of natural products.[12] The perspective of our complexes in RCM is demonstrated for 1,7-octadiene (Table 3). Once again, the activity depends on the N-heterocyclic carbene ligand. Compound **1** is more active than the chiral complex (*R,R*)-**3** at room temperature. Nevertheless, all compounds including the chiral derivatives show quantitative yields at elevated temperatures.

Table 3. RCM of 1,7-octadiene.[a]

Catalyst	T [°C]	t [min]	Yield [%]
(*R,R*)-**3**	25	10	7
1	25	10	51
1	60	10	>98
2	60	10	>98
(*R,R*)-**3**	60	10	>98
(*R,R*)-**4**	60	10	>98

[a] Reactions at 25 °C: Catalyst (6.30 µmol) in CH_2Cl_2 (0.20 mL); at 60 °C: Catalyst (6.30 µmol) in $ClCH_2CH_2Cl$ (0.20 mL); [1,7-octadiene]/[catalyst] = 50/1.

Our results clearly demonstrate that alkylidene complexes of ruthenium-containing N-heterocyclic carbenes complement and extend the known phosphane systems as catalysts in olefin metathesis.[11] The simple access to chiral metathesis catalysts appears promising for enantioselective metathesis reactions starting from prochiral olefins.[13]

Experimental Section

General procedure for complexes **1**–**5**: A solution of $[RuCl_2(PR_3)_2({=}CH\text{-}p\text{-}C_6H_4X)]$ (R = Ph or Cy; X = H or Cl) (1.0 mmol) in toluene (20 mL) was treated with a solution of the appropriate 1,3-dialkyl-imidazolin-2-ylidene (2.2 mmol) in toluene (5 mL) and stirred at room temperature for 45 min. The solution was filtered and then concentrated to about 2 mL. Upon addition of pentane (20 mL), a solid was precipitated which was separated from the mother liquor, dissolved in toluene (2 mL) and reprecipitated with pentane. This procedure was repeated twice. Finally, the complex was washed with pentane.

1: Yield: 86%; $C_{25}H_{38}Cl_2N_4Ru$: calcd: C 53.00, H 6.76, N 9.89; found: C 53.21, H 6.83, N 9.94.

2: Yield: 82%; $C_{37}H_{54}Cl_2N_4Ru$: calcd: C 61.14, H 7.49, N 7.71; found: C 61.23, H 7.56, N 7.87.

(*R,R*)-**3**: Yield: 83%; $C_{45}H_{46}Cl_2N_4Ru$: calcd: C 66.33, H 5.69, N 6.88; found: C 66.48, H 5.90, N 6.73.

(*R,R*)-**4**: Yield: 78%; $C_{61}H_{54}Cl_2N_4Ru$: calcd: C 72.18, H 5.36, N 5.52; found: C 72.34, H 5.46, N 5.45.

5: Crystals were obtained by slow diffusion of hexane into a solution of **5** in Et_2O/THF (5:1). Yield: 89%; $C_{24}H_{38}Cl_3N_4Ru$: calcd: C 47.96, H 6.37, N 9.32; found: C 48.13, H 6.33, N 9.24.

Received: April 30, 1998 [Z11799IE]
German version: *Angew. Chem.* **1998**, *110*, 2631–2633

Keywords: alkenes · carbenes · homogeneous catalysis · metathesis · ruthenium

---

[1] *Applied Homogeneous Catalysis with Organometallic Compounds* (Eds.: B. Cornils, W. A. Herrmann), VCH, Weinheim, **1996**.

[2] For a recent review see: M. Schuster, S. Blechert, *Angew. Chem.* **1997**, *109*, 2124–2144; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2036–2056.

[3] a) S. T. Nguyen, L. K. Johnson, R. H. Grubbs, *J. Am. Chem. Soc.* **1992**, *114*, 3974–3975; b) S. T. Nguyen, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1993**, *115*, 9858–9859; c) A. W. Stumpf, E. Saive, A. Demonceau, A. F. Noels, *J. Chem. Soc. Chem. Commun.* **1995**, 1127–1128; d) P. Schwab, M. B. France, J. W. Ziller, R. H. Grubbs, *Angew. Chem.* **1995**, *107*, 2179–2181; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2039–2041; e) W. A. Herrmann, W. C. Schattenmann, O. Nuyken, S. C. Glander, *Angew. Chem.* **1996**, *108*, 1169–1170; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1087–1088. f) A. Demonceau, A. W. Stumpf, E. Saive, A. F. Noels, *Macromolecules* **1997**, *30*, 3127–3136.

[4] For general reviews see: a) W. A. Herrmann, C. Köcher, *Angew. Chem.* **1997**, *109*, 2256–2282; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2162–2187; b) M. Regitz, *Angew. Chem.* **1996**, *108*, 791–794; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 725–728.

[5] a) H. W. Wanzlick, H. J. Schönherr, *Angew. Chem.* **1968**, *80*, 154–155; *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 141–142; b) K. Öfele, *J. Organomet. Chem.* **1968**, *12*, P42; c) A. J. Arduengo III, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361–363.

[6] a) W. A. Herrmann, M. Elison, J. Fischer, C. Köcher, G. R. J. Artus, *Angew. Chem.* **1995**, *107*, 2602–2605; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2371–2374; b) W. A. Herrmann, L. J. Gooßen, C. Köcher, G. R. J. Artus, *Angew. Chem.* **1996**, *108*, 2980–2982; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2805–2807.

[7] Compound **5** is prepared analogously starting from $[RuCl_2(PPh_3)_2({=}CH\text{-}p\text{-}C_6H_4Cl)]$.

[8] Crystal data for **5**: $C_{25}H_{37}Cl_3N_4Ru$; $M_r = 601.02$; monoclinic; space group $P2_1/n$ (No. 14); $a = 9.8856(1)$, $b = 17.3298(4)$, $c = 16.5954(3)$ Å; $\beta = 94.3395(12)^\circ$; $V = 2834.90(9)$ Å^3; $Z = 4$; $F(000) = 1240$; $\rho_{calcd} = 1.408\,g\,cm^{-3}$; $\mu(Mo_{K\alpha}) = 8.6\,cm^{-1}$ (crystal size: $0.15 \times 0.10 \times 0.02$ mm); $T = 193$ K; λ $(Mo_{K\alpha}) = 0.71073$ Å; detector: Kappa CCD (Nonius); 9603 data measured ($4.6^\circ < \theta < 25.1^\circ$), unique data = 4911; 3894 observed data $[I > 2.0\sigma(I)]$; hydrogens refined (U_{iso}); $N_{ref} = 4911$, $N_{par} = 446$; $R_1 = 0.049$, $wR_2 = 0.081$, $GOF = 1.021$; $w = 1/[\sigma^2(F_o^2) + (0.0379\,P)^2 + 1.3899\,P]$ with $P = (F_o^2 + 2\,F_c^2)/3$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101497 ; copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[9] A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, C34.

[10] P. Schwab, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1996**, *118*, 100–110.

[11] W. A. Herrmann, W. C. Schattenmann, T. Weskamp (Hoechst R&T), DE 19815275.2, **1998**.

[12] a) Z.Yang, Y. He, D. Vourloumis, H. Vallberg, K. C. Nicolaou, *Angew. Chem.* **1997**, *109*, 170–172; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 166–168; b) D. Meng, D. S. Su, A. Balog, P. Bertinato, E. J. Sorensen, S. J. Danishefsky, Y. H. Zheng, T. C. Chou, L. He, S. B. Horwitz, *J. Am. Chem. Soc.* **1997**, *119*, 2733–2734; c) D. Schinzer, A. Limberg, A. Bauer, O. M. Böhm, M. Cordes, *Angew. Chem.* **1997**, *109*, 543–544; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 523–524; d) A. Fürstner, K. Langemann, *Synthesis* **1997**, 792–803.

[13] a) O. Fujimura, R. H. Grubbs, *J. Am. Chem. Soc.* **1996**, *118*, 2499–2500; b) J. B. Alexander, D. S. La, D. R. Cefalo, A. H. Hoveyda, R. R. Schrock, *J. Am. Chem. Soc.* **1998**, *120*, 4041–4042.

The Stability of the Oxidation State +4 in Group 14 Compounds from Carbon to Element 114**

Michael Seth, Knut Faegri, and Peter Schwerdtfeger*

Dedicated to Professor Warren R. Roper
on the occasion of his 60th birthday

With the recent production of the transactinide isotopes $^{269}(110)$, $^{271}(110)$, $^{273}(110)$, $^{272}(111)$, and $^{277}(112)$,[1, 2] the synthesis of the next superheavy elements 113 and 114 in the near future seems to be feasible.[3] For elements with a lifetime in the second range, atom-at-a-time chemistry can give valuable insight into their chemical behavior,[4, 5] and very recently experiments have been carried out on element 106 (seaborgium) by Schädel et al. at the Gesellschaft für Schwerionenforschung (GSI) in Darmstadt.[6] Macroscopic and microscopic calculations predict an island of nuclear stability near nuclear charge $Z = 114$ and neutron number $N = 180$ with an α-decay half-life of 12 h.[7] However, it is unlikely that such a large neutron number can be achieved with current nuclear fusion techniques. Quantum-chemical calculations are therefore presently the only way to accurately predict the physical and chemical behavior of superheavy elements.[8, 9]

Gas-phase transactinide chemistry is generally carried out in high oxidation states because the resulting volatility allows separation from the other nuclides. By comparison with the known chemistry of the Group 14 elements, the most likely oxidation states of element 114 (eka-lead) are +2 and +4. Grant and Pyper predicted heats of formation for di- and tetravalent compounds of element 114 empirically with Dirac–Fock data.[10] This study suggests a rather low stability of the oxidation state +4, in agreement with the general trend of decreasing stability of the higher oxidation state on going to the heavier main group elements (often termed the inert pair effect).[11] However, high-level relativistic calculations are necessary to decide whether a compound like $(114)F_4$ is thermodynamically stable.

We carried out spin–orbit coupled relativistic pseudopotential calculations for the hydrides, chlorides, and fluorides of element 114 [$(114)X_2$ and $(114)X_4$ (X = H, F, Cl)], as well as four-component Dirac–Fock (DF) calculations for element 114 and the hydrides $(114)H_2$ and $(114)H_4$.[12–16] The nonrelativistic and spin–orbit coupled relativistic pseudopotentials were obtained by a multielectron fitting procedure to calculated numerical (Hartree–Fock) HF and DF data. Electron correlation was included at the coupled cluster level CCSD(T) and at the second-order Møller–Plesset level (MP2). If accurate dissociation energies were not known for the lighter Group 14 homologues Pb, Ge, and Sn, these were determined by ab initio calculations with the pseudopotentials and basis sets of Stoll et al.[17] Optimization of the structures at the MP2 level led to T_d symmetry for $(114)X_4$ and C_{2v} symmetry for $(114)X_2$. Single-point CCSD(T) calculations were carried out with the optimized MP2 geometries. All relativistic calculations for CH_2 and CH_4 were carried out by using the nonrelativistic optimized geometry.[18, 19]

Table 1 compares the atomic properties of element 114 calculated at the CCSD(T) level with experimental data for Pb. The ground state of element 114 is best described by *jj* coupling ($J = 0$). The MCDF calculations show that admixtures from $p_{3/2}$ orbitals are small. The coefficients of the configuration state wavefunctions are 0.9957 for the $p_{1/2}^2$ configuration (cf. the nonrelativistic limit of $+\sqrt{2/3}$) and -0.0929 for the $p_{3/2}^2$ configuration (nonrelativistic limit $-\sqrt{1/3}$). Hence, the ground-state configuration is a closed-shell system. However, in agreeement with the other Group 14 elements, we use the term symbol $^3P_0$ in the following, even though the $^1S_0$ contribution is important in the $J = 0$ ground state of element 114. At the CCSD(T) level of theory the electron affinity of element 114 is zero (Figure 1 a), that is, element 114 cannot accomodate an extra

---

[*] Prof. Dr. P. Schwerdtfeger, Dr. M. Seth
Department of Chemistry, University of Auckland
Private Bag 92019, Auckland (New Zealand)
Fax: (+64) 9-3737422.
E-mail: schwerd@ccu1.auckland.ac.nz

Prof. Dr. K. Faegri
Department of Chemistry, University of Oslo
P.O. Box 1033 Blindern, N-0315 Oslo 3 (Norway)

[**] This work was supported by the European Science Foundation (REHE program), the Auckland University Research Committee, and the Marsden Fund managed by the Royal Society of New Zealand (contract number 96-UOA-PSE-0081).