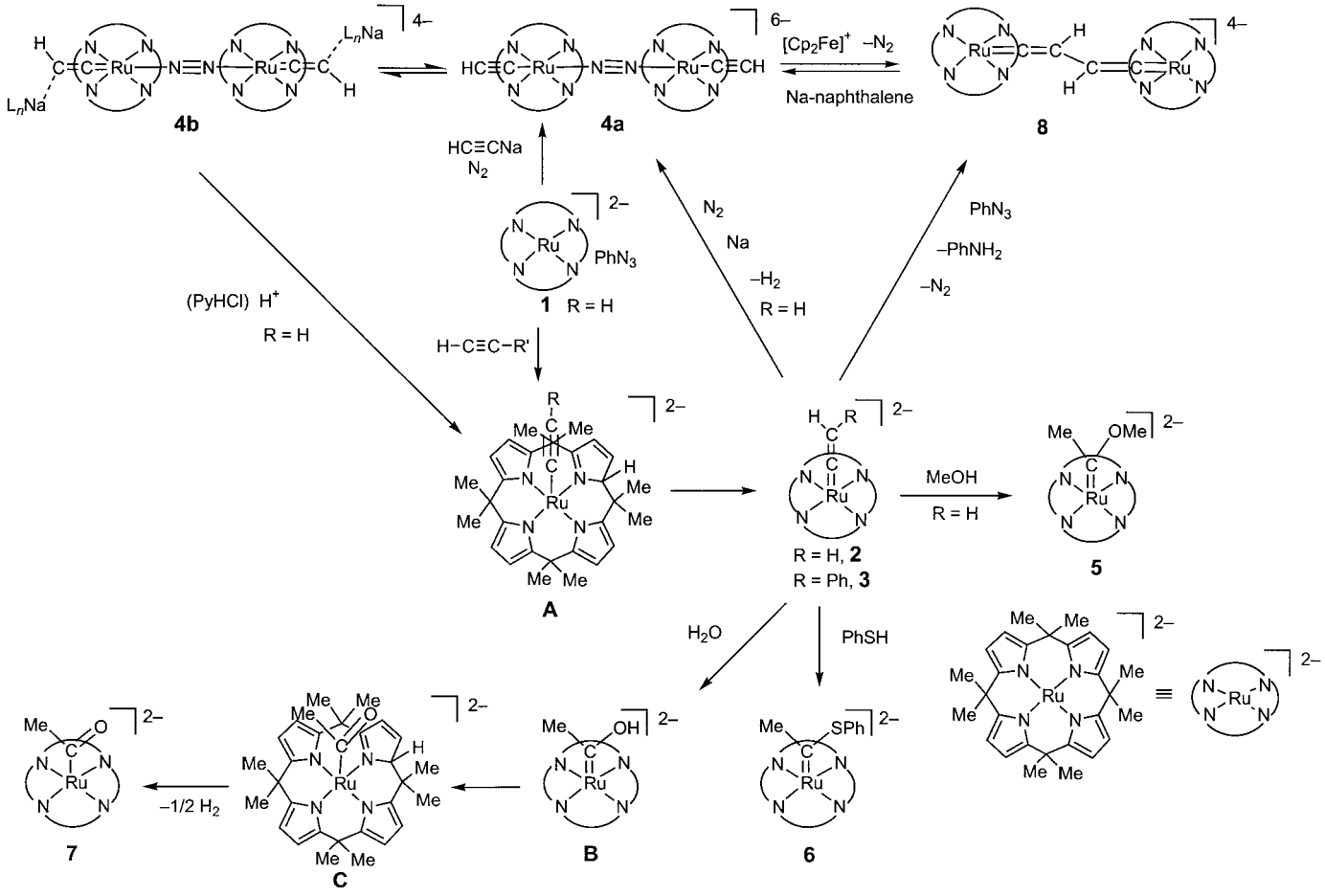
Acetylenes Rearranging on Ruthenium–Porphyrinogen and Leading to Vinylidene and Carbene Functionalities**

Lucia Bonomo, Christine Stern, Euro Solari, Rosario Scopelliti, and Carlo Floriani*

The *meso*-octaalkylporphyrinogen tetraanion[1] has allowed the use of standard organometallic methodologies to be extended to a metalla-macrocycle, enabling the formation of unusual functionalities and the discovery of novel reactivities in a nonconventional organometallic environment. Herein we are specifically referring to the [Ru=C] group,[2] which can be found in a variety of forms throughout organometallic chemistry, and yet has a very limited presence in macrocyclic chemistry. This can be exemplified by the derivatization of Ru–porphyrin[3] and Ru–tmtaa[4] complexes (tmtaa = dibenzotetramethyltetraaza[14]annulene), where the Ru–carbene unit is produced from diazoalkanes[3, 4] or by other methods.[3c, 5]

Herein we report how we synthesized the [Ru=C=CHR] unit by acetylene rearrangements[2, 6] in the reaction with **1** (see Scheme 1), and how we then converted the [Ru=C=CHR] unit into a variety of carbene and metallacumulene structures.[2, 6] The paper most related to our work reports the reaction of Ru–porphyrin with ethyne to produce



Scheme 1. The synthesis and reactivity of the porphyrinogen–Ru–vinylidene functionality. Complexes **1**–**8** were isolated and fully characterized. Complexes **A**–**C** are speculative.

a μ-biscarbene.[7] Although these functionalities have various precedents in the case of cyclopentadienyl, phosphine, arene,[2, 6, 8] and some amine[9] ligands, they are absent in the macrocyclic ruthenium chemistry. The parent Ru-*meso*-octamethylporphyrinogen **1**[10] was prepared according to the known procedure for this class of compounds.[1] For the sake of clarity, compounds in Scheme 1 are reported in their anionic form, rather than in the ion-pair form usually identified in the solid state. Acetylene and phenylacetylene react smoothly with **1** to form **2** and **3**,[10] respectively. Complexes **2** and **3** have been fully characterized, including the X-ray analysis of **2** (Ru=C 1.738(5), C=C 1.356(7) Å).[2a]

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Unlike in the reactions reported for the conventional Ru–organometallic fragments,[2, 6, 8] the reaction discussed here, possibly, proceeds by a different pathway, which does not involve in a preliminary stage any η^2 complexation of the alkyne.[11] Diphenylacetylene or other internal alkynes do not react with **1**. For **1**, we propose the preliminary protonation of the porphyrinogen skeleton[12] followed by the binding of the acetylide anion to the metal (see intermediate **A** in Scheme 1), then rearrangement to the vinylidene functionality[2, 6, 8] upon proton transfer from the porphyrinogen ligand. The protonation of Ni–porphyrinogen by PhC≡CH[12] gave strong support to the hypothesis that the porphyrinogen ligand assists the proton transfer reaction; the reaction of **1** with CH≡CNa in THF also supports this hypothesis. The reaction gave a compound which displays different structures in the solid state, depending on the crystallization solvent. The crystallization from dimethoxyethane (DME) led to **4a**, while the crystallization from THF gave the **4b** form. Both of these compounds contain the same core $[\{Ru(Me_8N_4)\}_2(\mu\text{-}N_2)(\mu\text{-}Na)_4]^{2-}$, where the two Ru–porphyrinogen moieties are bridged by four sodium cations and a dinitrogen molecule.[13] Although structural details are only given for **4b**, it is useful to stress the structural differences between **4a** and **4b**. The form **4a** contains the acetylide functionalities (Ru–C 1.875(3); C≡C 1.185(4) Å) with two noninteracting sodium countercations $[Na(dme)_3]^+$, while in **4b** (see Figure 1),[14] the terminal functionalities have the anionic vinylidene form, with the $[Na(thf)_5]^+$ cations associated with them. In the latter case, the solvated sodium cation plays the role of an incoming electrophile (Ru=C 1.807(9), C=C 1.314(12) Å). Both forms **4a** and **4b**, when dissolved in $[D_8]$THF (C_4D_8O), gave a ^{1}H NMR spectrum consistent with the **4b** structure. Complex **4b** in solution is easily protonated to **2**.

The vinylidene unit in **2** and **3** offers the synthetic entry to heterocarbenes and cumulenes otherwise inaccessible with macrocyclic ligands. Such synthetic versatility has been demonstrated in the reaction of **2** with methanol and thiophenol, leading to **5** and **6**, respectively.[10] The reaction proceeds according to the vinylidene polarization with the proton reacting at the β carbon, followed by the nucleophile attacking the α carbon.[2, 6] Unlike for many organometallic counterparts, the reaction occurs with a very high degree of selectivity and high yield. The characterization of **5** (Ru–C 1.80(1), C–OMe 1.38(1) Å) and **6** is given in the Supporting Information. The reaction of **2** with H_2O follows the pathway shown for the other protic substrates (Scheme 1, intermediates **B** and **C**),[2, 6c] except that the final compound (**7**) has an acyl functionality which has been formed in conjunction with the oxidation of Ru^{II} to Ru^{III}, as depicted in Scheme 1. The complex is paramagnetic ($\mu_{eff} = 1.85$ BM at 293 K, $\tilde{\nu}_{CO} = 1577\ cm^{-1}$), and has been characterized in the solid state by X-ray analysis (Ru–C 1.91(1), C=O 1.24(1) Å).

The vinylidene functionality in **2** allows a versatile derivatization of the Ru–porphyrinogen, thus providing an easy way to produce a dimetallabisvinylidene. The oxidation of **2** has been carried out using PhN_3, which was reduced to aniline. The reaction led to **8**[10] (Scheme 1; Ru–C 1.735(14), C–C 1.338(16), C–C 1.473(17) Å) by the oxidative coupling of the vinylidene functionality. The oxidation of **4b** using the oxidizing agent $[Cp_2Fe]^+$ gave **8** equally effectively (in solution **4a** converts into **4b**, see above). The latter reaction is reversible, since the reduction of **8** with Na–naphthalene gave back **4b** with the cleavage of a C–C single bond. The analytical and spectroscopic characterization of **8** is given in the Experimental Section while the X-ray structure, showing one out of the four sodium cations sandwiched between two porphyrinogen units, is displayed in Figure 2,[14] the other

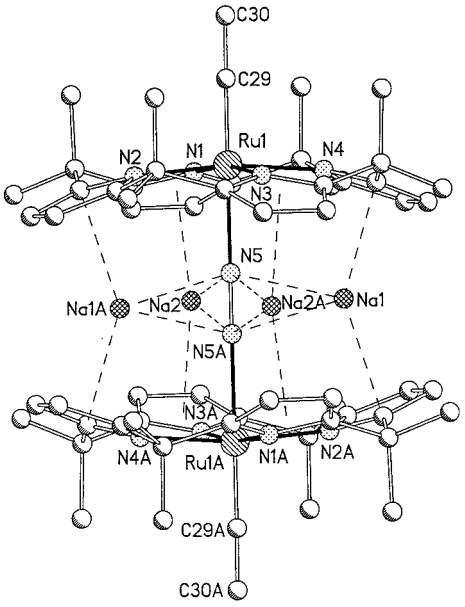

Figure 1. Molecular structure of **4b** (hydrogen atoms and $[Na(thf)_5]^+$ ions are omitted for clarity). Selected distances [Å] and angles [°]: Ru1-N1–4$_{average}$ 2.119(8), Ru1-C29 1.807(9), Ru1-N5 2.251(8), C29-C30 1.314(12), N5-N5A 1.284(15), Na1···N5 2.573(10), Na1···N5A 2.609(9), Na2···N5 2.542(9) Na2···N5A 2.631(9); C29-Ru1-N5 179.2(4), N5A-N5-Ru1 177.4(10), C30-C29-Ru1 177.9(9). The A indicates the following symmetry operation: $-x+1, -y+1, -z+1$.

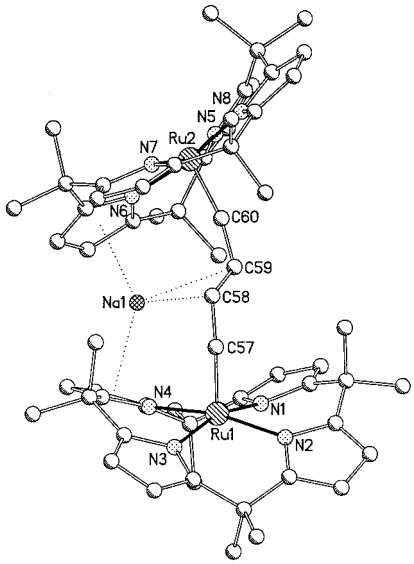

Figure 2. Molecular structure of compound **8** (hydrogen atoms, solvated sodium atoms, and solvent molecules are omitted for clarity). Selected distances [Å] and angles [°]: Ru1-N$_{average}$ 2.047(10), Ru1-C57 1.735(14), Ru2-N$_{av}$ 2.033(12), Ru2-C60 1.734(14), C57-C58 1.338(16), C58-C59 1.473(17), C59-C60 1.326(17), Na1···C58 2.762(13), Na1···C59 2.796(14); C59-C60-Ru2 166.2(12), C58-C57-Ru1 164.6(11).

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three sodium cations being present as solvent-separated cations. Complex **8** can provide an entry to dimetallacumulene and dimetallacarbene compounds.

Experimental Section

1: $[RuCl_2(cod)]$ (6.19 g, 22.0 mmol; COD = 1,5 cyclooctadiene) was added to a solution of $[Me_8N_4Na_4(thf)_4]$ (17.8 g, 22.0 mmol) in dimethoxyethane (DME; 300 mL). The reaction mixture was heated to reflux for 24 h and the NaCl was filtered off. The resulting solution was allowed to stand at $-20\,^{\circ}C$ giving an orange crystalline product which was collected and dried in vacuo (11 g, 45 %). Crystals suitable for X-ray diffraction were grown in DME. ^1H NMR (400 MHz, $[D_6]$DMSO, 25 °C, TMS): $\delta = 5.74$ (s, 8H; C_4H_2N), 3.41 (s, 24H; DME), 3.23 (s, 36H; DME), 1.43 (s, 24H; CH_3); ^{13}C NMR (400 MHz, $[D_6]$DMSO, 25 °C): $\delta = 146.1$, 100.1, 71.0, 58.0, 39.1, 36.9; elemental analysis calcd (%) for $\mathbf{1}\cdot 6(C_4H_{10}O_2)$, $C_{52}H_{92}N_4Na_2O_{12}Ru$ (1112.4): C 56.15, H 8.34, N 5.04; found: C 55.91, H 8.40, N 4.96.

2: A solution of $\mathbf{1}\cdot 6(C_4H_{10}O_2)$ (1.50 g, 1.35 mmol) in THF (100 mL) was stirred under an acetylene atmosphere at room temperature for 24 h and then the solvent was removed in vacuo. The residue was treated with *n*-hexane (50 mL) giving an amber solid which was collected and dried in vacuo (0.93 g, yield 88 %). Crystals suitable for X-ray diffraction were grown in a mixture of THF/*n*-hexane. ^1H NMR (400 MHz, $[D_6]$benzene/$[D_8]$THF, 25 °C, TMS): $\delta = 6.46$ (s, 8H; C_4H_2N), 3.06 (s, 8H; dimethoxyethane (DME)), 2.98 (s, 12H; DME), 2.78 (s, 2H; CH_2), 1.91 (s, 12H; CH_3), 1.81 (s, 12H; CH_3); ^{13}C NMR (400 MHz, $[D_6]$benzene/$[D_8]$THF, 25 °C): $\delta =$ 300.28, 145.07, 102.44, 94.44, 71.51, 58.84, 39.49, 38.18, 33.21; IR (nujol, $\tilde{\nu}_{max}$): 1557.6 cm^{-1}; elemental analysis calcd (%) for $\mathbf{2}\cdot 2(C_4H_{10}O_2)$, $C_{38}H_{54}N_4Na_2O_4Ru$ (777.9): C 58.67, H 7.00, N 7.20; found: C 59.0, H 6.92, N 7.28.

4a:[10] HC_2Na (86 mg, 1.8 mmol) was added to a solution of **1** (1.0 g, 0.9 mmol) in THF (100 mL) at room temperature. The reaction mixture immediately became light yellow. After 1 h of stirring, the solution was evaporated to dryness and the residue was washed with Et_2O (50 mL) to give a white solid which was collected and dried in vacuo (0.59 g, 77 %) (IR; $\tilde{\nu}_{C\equiv C}$, 2000 cm^{-1}). Crystals suitable for X-ray diffraction were grown in DME and have a different degree of solvation by THF than the noncrystalline product. ^1H NMR (400 MHz, $[D_8]$THF, 25 °C, TMS): $\delta =$ 5.76 (s, 8H; C_4H_2N), 5.68 (s, 8H; C_4H_2N), 3.47 (s, 24H; DME), 3.31 (s, 36H; DME), 2.19 (s, 2H; CH), 1.63 (s, 12H; CH_3), 1.58 (s, 12H; CH_3), 1.24 (s, 12H; CH_3), 1.18 (s, 12H; CH_3); elemental analysis calcd (%) for $\mathbf{4}\cdot 6(C_4H_{10}O_2)$, $C_{84}H_{126}N_{10}Na_6O_{12}Ru_2$ (1808.0): C 55.80, H 7.02, N 7.75; found: C 55.85, H 7.05, N 7.67.

8: Method A: PhN_3 (0.61 mg, 5.14 mmol) was added to a solution of $\mathbf{2}\cdot 2(C_4H_{10}O_2)$ (4.0 g, 5.14 mmol) in THF (100 mL). The reaction mixture was stirred at room temperature overnight, then evaporated to dryness and the solid residue triturated with *n*-hexane (100 mL) to give a brown solid which was collected and dried in vacuo (1.26 g, 85 %). Crystals suitable for X-ray diffraction were grown in a mixture of THF/dioxane. ^1H NMR (400 MHz, $[D_5]$pyridine, 25 °C, TMS): $\delta = 6.54$ (s, 16H; C_4H_2N), 3.66 (s, 2H; CH), 3.48 (s, 16H; DME), 3.25 (s, 24H; DME), 1.90 (s, 24H; CH_3), 1.46 (s, 24H; CH_3); elemental analysis calcd (%) for $\mathbf{8}\cdot 4(C_4H_{10}O_2)$, $C_{76}H_{106}N_8Na_4O_8Ru_2$ (1553.8): C 58.75, H 6.88, N 7.21; found: C 58.61, H 6.24, N 7.15. Method B: $[Cp_2Fe]^+BPh_4^-$ (1.9 g, 3.38 mmol) was added to a solution of $\mathbf{4}\cdot 4(C_4H_{10}O_2)\cdot 2(C_4H_8O)$ (2.8 g, 1.69 mmol) in THF (150 mL). The reaction mixture was stirred at room temperature overnight, then was evaporated to dryness and the solid residue triturated with *n*-hexane (100 mL) to give a brown solid which was collected and dried in vacuo (1.73 g, 76 %). ^1H NMR (400 MHz, $[D_5]$pyridine, 15 °C, TMS): $\delta = 6.54$ (s, 16H; C_4H_2N), 3.66 (s, 2H; CH), 3.48 (s, 16H; DME), 3.25 (s, 24H; DME), 1.90 (s, 24H; CH_3), 1.46 (s, 24H; CH_3); elemental analysis calcd (%) for $\mathbf{8}\cdot 4(C_4H_{10}O_2)$, $C_{76}H_{106}N_8Na_4O_8Ru_2$: C 58.75, H 6.88, N 7.21; found: C 58.73, H 6.21, N 7.09.

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[1] C. Floriani, R. Floriani-Moro in *The Porphyrin Handbook*, *Vol. 3* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, New York, **2000**; a) Chap. 24, p. 385; b) Chap. 25, p. 405.

[2] a) A. F. Hill in *Comprehensive Organometallic Chemistry II*, *Vol. 7* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Elsevier, Oxford, **1995**, Chap. 6, p. 299; b) M. A. Bennett, K. Khan, E. Wenger in *Comprehensive Organometallic Chemistry II*, *Vol. 7* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Elsevier, Oxford, **1995**, Chap. 8, p. 473; c) M. A. Bennett in *Comprehensive Organometallic Chemistry II*, *Vol. 7* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Elsevier, Oxford, **1995**, Chap. 9, p. 549.

[3] a) J. P. Collman, C. E. Barnes, P. N. Swepston, J. A. Ibers, *J. Am. Chem. Soc.* **1984**, *106*, 3500; b) J. P. Collman, P. J. Brothers, L. McElwee-White, E. Rose, L. J. Wright, *J. Am. Chem. Soc.* **1985**, *107*, 4570; c) J. P. Collman, P. J. Brothers, L. McElwee-White, E. Rose, *J. Am. Chem. Soc.* **1985**, *107*, 6110.

[4] a) A. Klose, E. Solari, C. Floriani, S. Geremia, L. Randaccio, *Angew. Chem.* **1998**, *110*, 155; *Angew. Chem. Int. Ed.* **1998**, *37*, 148; b) A. Klose, E. Solari, J. Hesschenbrouck, C. Floriani, N. Re, S. Geremia, L. Randaccio, *Organometallics* **1999**, *18*, 360.

[5] The two single Ru–vinylidenes known in porphyrin chemistry come from different (see ref. [3c]) or quite convoluted reactions: see Y. W. Chan, M. W. Renner, A. L. Balch, *Organometallics* **1983**, *2*, 1888; A. L. Balch, Y. W. Chan, M. M. Olmstead, M. W. Renner, F. E. Wood, *J. Am. Chem. Soc.* **1988**, *110*, 3897.

[6] a) M. I. Bruce, *Chem. Rev.* **1991**, *91*, 197; b) M. I. Bruce, *Chem. Rev.* **1998**, *98*, 2797; c) C. Bruneau, P. H. Dixneuf, *Acc. Chem. Res.* **1999**, *32*, 311.

[7] N. Rajapakse, B. R. James, D. Dolphin, *Can. J. Chem.* **1990**, *68*, 2274.

[8] a) C. Grünwald, O. Gevert, J. Wolf, P. González-Herrero, H. Werner, *Organometallics* **1996**, *15*, 1960; b) H. Katayama, F. Ozawa, *Organometallics* **1998**, *17*, 5190; c) M. A. Jiménez-Tenorio, M. Jiménez-Tenorio, M. C. Puerta, P. Valerga, *Organometallics* **2000**, *19*, 1333; d) W.-H. Leung, K.-K. Lau, Q. Zhang, W.-T. Wong, B. Tang, *Organometallics* **2000**, *19*, 2084; e) J. Wolf, W. Stüer, C. Grünwald, O. Gevert, M. Laubender, H. Werner, *Eur. J. Inorg. Chem.* **1998**, 1827; f) H. Werner, A. Stark, M. Schultz, J. Wolf, *Organometallics* **1992**, *11*, 1126; g) H. Werner, A. Stark, P. Steinert, C. Grünwald, J. Wolf, *Chem. Ber.* **1995**, *128*, 49; h) M. Martin, O. Gevert, H. Werner, *J. Chem. Soc. Dalton Trans.* **1996**, 2275.

[9] a) S.-M. Yang, M. C.-W. Chan, K.-K. Cheung, C.-M. Che, S.-M. Peng, *Organometallics* **1997**, *16*, 2819; b) I. del Río, R. A. Gossage, M. S. Hannu, M. Lutz, A. L. Spek, G. van Koten, *Organometallics* **1999**, *18*, 1097.

[10] Syntheses of **1**, **2**, **4** (Method A), and **8** are in the Experimental Section while those of **3**, **4** (Methods B and C), **5**, **6**, and **7** are in the Supporting Information.

[11] a) Y. Wakatsuki, N. Koga, H. Werner, K. Morokuma, *J. Am. Chem. Soc.* **1997**, *119*, 360; b) J. Silvestre, R. Hoffmann, *Helv. Chim. Acta* **1985**, *68*, 1461; c) J. R. Lomprey, J. P. Selegue, *J. Am. Chem. Soc.* **1992**, *114*, 5518, and refs therein; d) Y. Wakatsuki, N. Koga, H. Yamazaki, K. Morokuma, *J. Am. Chem. Soc.* **1994**, *116*, 8105; e) I. de los Ríos, M. Jiménez-Tenorio, M. C. Puerta, P. Valerga, *J. Am. Chem. Soc.* **1997**, *119*, 6529; f) R. M. Bullock, *J. Chem. Soc. Chem. Commun.* **1989**, 165.

[12] L. Bonomo, E. Solari, C. Floriani, A. Chiesi-Villa, C. Rizzoli, *J. Am. Chem. Soc.* **1998**, *120*, 12972.

[13] Dinitrogen binding to Ru^{II} in such complexes, depending on the electronic density at the metal, is a quite common event: L. Bonomo, E. Solari, C. Floriani, unpublished results.

[14] Crystal structure analysis of **4b**: $[C_{60}H_{66}N_{10}Ru_2][Na]_4[Na(C_4H_8O)_5]_2$, $M_r = 1988.35$, monoclinic, space group $P2_1/n$, $a = 13.016(3)$, $b = 29.446(6)$, $c = 13.102(3)$ Å, $\beta = 90.42(3)^{\circ}$, $V = 5021.5(17)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.315$ g cm^{-3}, $F(000) = 2100$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71070$ Å), μ ($Mo_{K\alpha}$) = 0.388 mm^{-1}; crystal dimensions $0.20 \times 0.18 \times 0.12$. Diffraction data were collected on a mar345 Imaging Plate at 143 K. The structure was solved using direct methods and refined using the full-matrix least-squares on F^2 with all non-H atoms anisotropically defined. For 2795 observed reflections ($I > 2\sigma(I)$) and 581 parameters, the conventional R is 0.0643 ($wR2 = 0.1849$ for 6011 independent reflections). Crystal structure analysis of **8**: $[C_{60}H_{66}N_8Ru_2][Na]$-$[Na(C_4H_{10}O_2)(C_4H_8O_2)_{0.5}][Na(C_4H_8O)(C_4H_8O_2)_{0.5}][Na(C_4H_8O_2)_2$-$(C_4H_{10}O_2)(C_4H_8O)]\cdot 2(C_4H_8O)$, $M_r = 1926.28$, monoclinic, space group $P2_1/c$, $a = 18.547(4)$, $b = 26.947(5)$, $c = 21.668(4)$ Å, $\beta = 114.19(3)^{\circ}$, $V = 9878(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.295$ g cm^{-3}, $F(000) = 4072$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71070$ Å), μ ($Mo_{K\alpha}$) = 0.387 mm^{-1}; crystal dimensions $0.23 \times 0.18 \times 0.15$. Diffraction data were collected on a mar345 Imaging Plate at 143 K. The structure was solved by means of

direct methods and refined using the full-matrix least-squares on F^2 with all non-H atoms anisotropically defined (except the external sodium atom and the solvent molecules). For 4426 observed reflections ($I > 2\sigma(I)$) and 921 parameters, the conventional R is 0.0879 ($wR2 = 0.2670$ for 10835 independent reflections). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-154158 (**4**) and CCDC-154159 (**8**). 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).

A Readily Available and User-Friendly Chiral Catalyst for Efficient Enantioselective Olefin Metathesis**

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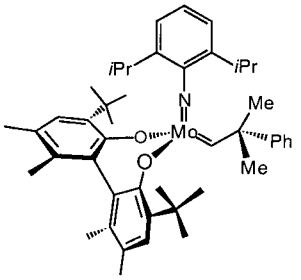
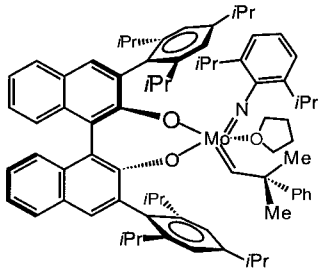
We recently reported the synthesis and utility of various Mo-based chiral catalysts that promote enantioselective olefin metathesis.[1] These complexes, represented by (*S*)-**1**[2] and (*R*)-**2**[3], are the only existing class of chiral catalysts that efficiently and selectively promote the formation of optically pure or enriched carbo- and heterocycles through asymmetric ring-closing[4] and ring-opening metathesis (ARCM and AROM, respectively).[5] One notable difference between **1** and **2** is that biphenolate **1** initiates selective ARCM of five-membered rings and binaphtholate **2** is often the catalyst of choice for the enantioselective synthesis of six-membered analogues.[3]

From a practical point of view, binaphthol-based systems (e.g., **2**) have a significant advantage: the synthesis of the optically pure diolate begins from the inexpensive and commercially available (*R*)- or (*S*)-binaphthol.[6] In contrast, access to the optically pure biphenol ligand in **1** and its derivatives requires resolution of the racemic samples by fractional crystallization of the derived phosphorus(v) mentholates.[2] We therefore judged that a chiral Mo complex that bears a "biphenol-type" ligand, but is synthesized from the readily available optically pure binaphthol, would be an important and valuable addition to this unique class of chiral catalysts. We also suspected that such a catalyst could exhibit greater generality: its reactivity and selectivity trends may overlap those exhibited by the biphenol- (e.g., **1**) *and* binaphthol-based complexes (e.g., **2**).

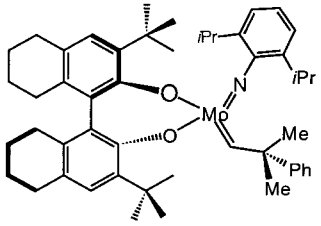
Herein, we report the synthesis, structure, and synthetic utility of chiral complex **3**, a Mo catalyst that resembles a biphenol-based catalyst (**1**) but, similar to **2**, is easily prepared from optically pure binaphthol. We demonstrate that complex **3** offers a solution to the important problem of practicality in Mo-catalyzed asymmetric olefin metathesis. The new catalyst may be prepared from commercially available starting materials and can be used in situ, without isolation, to effect enantioselective olefin metathesis.



(*S*)-**1**



(*R*)-**2**



(*R*)-**3**

Preparation of chiral catalyst **3** (Scheme 1) begins with catalytic hydrogenation of commercially available, optically pure (*R*)-**4** in the presence of PtO_2[7] under 100 psi (6.9 atm, 690 KPa) H_2 in glacial acetic acid (HOAc).[8] In a 20 g (69.9 mmol) scale reaction, the desired octahydrobinaphthol **5** is formed in >98% yield (cream-colored powder).[9] Installation of *t*Bu groups at the C2 and C2′ sites is carried out by acid-catalyzed alkylation with isobutylene, a procedure that involves the difficult separation of the desired functionalized binaphthol from adventitious oligoisobutylenes; pure dialkylated product is obtained after chromatography on silica gel in 40% yield. However, when the unpurified mixture is directly treated with 2 equivalents of KH, the derived dipotassium salt (*R*)-**6** is isolated in 85% yield. Through this procedure, oligoisobutylene impurities are removed by washing with pentane. The resulting dipotassium salt (*R*)-**6** (soon to be commercially available through Strem) does not need further purification before it is employed in the synthesis of **3**.[10]

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