Note

N-Functionalised heterocyclic dicarbene complexes of silver: Synthesis and structural studies

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Abstract

A range of new diimidazolium salts, held together by an alkyl unit and bearing alcohol pendant arms on their nitrogen, was synthesized. A short modular reaction pathway leads to the N-heterocyclic carbene (NHC) precursors, differing by the flexibility of the bridge, the steric bulk of substituents in α-position of the OH groups and the anions. Treatment of diimidazolium salts with Ag_2O yields $Ag^I(carbene)_2$ complexes. The related trimethylene-bridged bis-NHC silver complexes **6** and **7** were crystallised with di-tosylate and di-hexafluorophosphate anions, respectively. Their X-ray structures revealed dimeric species, involving two ligands with different arrangements around the Ag cations, leading to crossed and parallel conformations.
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1. Introduction

Since the pioneer work on metal N-heterocyclic carbenes (NHCs) by Öfele and Wanzlick, intensive activity research has been focused on the organometallic chemistry of this class of ligands [1–3]. Strong nucleophilic character, low tendency for ligand dissociation and ability to stabilise high- and low-valent metals, have made NHC-complexes attractive targets in contemporary catalysis [4–7]. In the last decade, a large number of reports described the unprecedented activity of carbene complexes in important reactions, such as Pd-catalysed Heck- and Suzuki-coupling, Co-catalysed ethylene copolymerisation, Ru-catalysed olefin metathesis and Rh-catalysed hydrosilylation [8–18].

We are interested in the use of polydentate bis-NHC ligands. For this purpose, we describe the preparation of several diimidazolium salts, bridged by aliphatic chains and bearing alcohol pendant arms, with different substitu-ents in α-position of the OH functions. We also report structural studies of two original dimeric silver complexes.

2. Results and discussion

2.1. Synthesis of NHC precursors bearing alcohol arms

Alkane-bridged bis-imidazolium salts **2**, **3** and **5** were synthesized in two steps (Scheme 1). The first one corresponds to a ring-opening of an epoxide, a method applied by Arnold for the synthesis of asymmetric imidazolium precursors of mixed alkoxide-carbene ligands [19]. Quaternisation of the alcohol-substituted imidazoles **1** or **4** by reaction with one half equivalent of the appropriate dibromoalkane or ditosylate diol lead to precursor ligands **2**, **3** and **5** in quantitative yield.

Main characteristics in ^1H spectra are resonances for the imidazolium protons (9.08 ppm (**2**), 9.24 ppm (**3**) and 9.17 ppm (**5**)). In ^{13}C spectra, corresponding imidazole carbon resonances are located at 137.4 ppm (**2**), 138.4 ppm (**3**) and 137.1 ppm (**5**). FAB-MS spectra obtained from
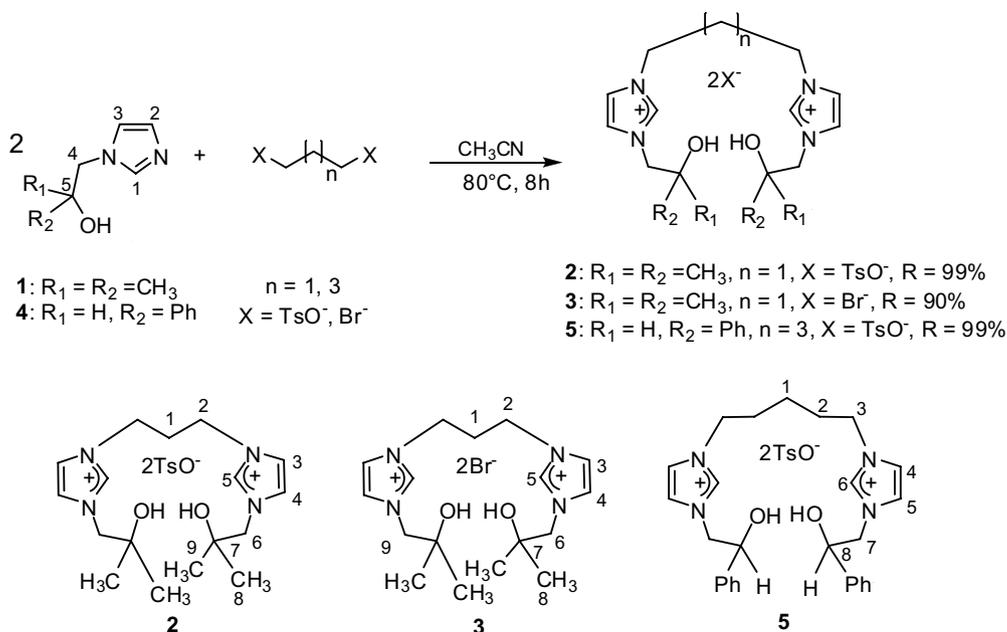
Scheme 1. Synthesis of alcohol-functionalised diimidazolium salts **2**, **3** and **5**.

the ditosylate derivatives exhibit peaks corresponding to $[M-TsO^-]^+$ (m/z 493 (**2**) and 617 (**5**)) and $[M-2TsO^--H^+]^+$ (m/z 321 (**2**) and 445 (**5**)), respectively. FAB-MS spectrum of **3** shows only the $[M-Br^-]^+$ cation at m/z 401.

2.2. Synthesis and characterisation of silver(I)–carbene complexes

$Ag^I(carbene)_2$ complexes **6**, **8** and **9** were prepared by deprotonation of alcohol-functionalised bis-imidazolium salts **2**, **3** and **5**, with the mild base Ag_2O at 50 °C in dry DMSO or methanol in the presence of 4 Å MS (Scheme

2). Ion exchange of complex **6** with NH_4PF_6 in methanol afforded complex **7**.

Notable features in ^1H spectra of complexes **6**–**9** are the resonances for alcohol functions (4.84 ppm (**6**, **7**), 5.05 ppm (**8**) and 5.84 ppm (**9**)). Arnold reported that reaction of alcohol-functionalised imidazolium halides with Ag_2O can lead to deprotonation of C–H and O–H protons, yielding halide free Ag(I)–NHC–alkoxide complexes [19,20]. In our case, Ag_2O is not basic enough to deprotonate the alcohol functions; the chemical behaviour of the remaining acidic H-atom of the OH function is as it is bridged between the alkoxide and carbene groups, making it less easy to remove [20].
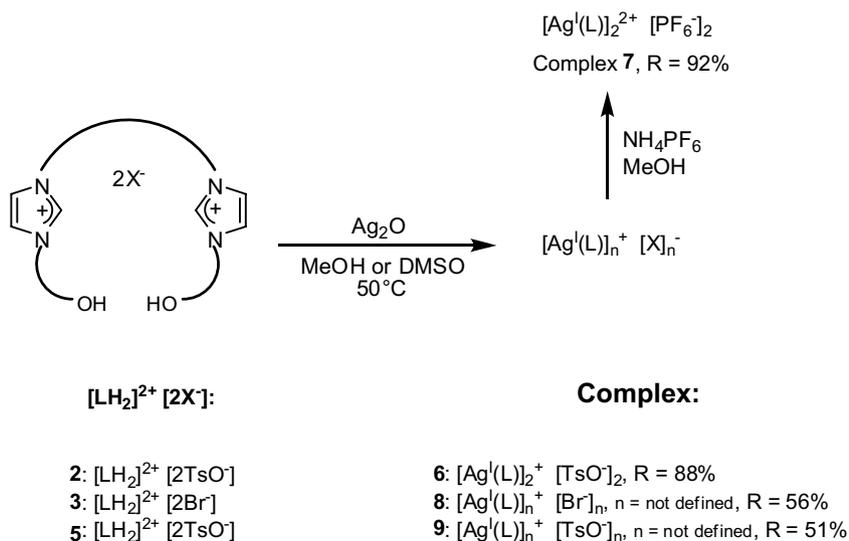
Scheme 2. Synthesis of silver complexes **6**–**9**.

In the ^{13}C spectrum of **6** synthesized in methanol, the carbene resonance appears at two doublets (181.3 ppm) with coupling constants ($J_{C-Ag}^{107} = 181.9$ Hz, $J_{C-Ag}^{109} = 209.0$ Hz), in the range of reported values [21]. The ^{13}C spectra of **6**, prepared in DMSO, and of **7–9** show only one doublet or a sharp signal (181.4 ppm (**6**), 180.2 ppm (**7**), 181.9 ppm (**8**) and 181.4 ppm (**9**)) for the carbonium carbon. The lack of silver–carbene coupling indicates the lability of the Ag–carbene bond in solution [22]. The presence of PF_6^- in complex **7** is confirmed by the ^{31}P spectrum (septuplet centered at -144.2 ppm, $J_{PF} = 716.8$ Hz). All the MS/FAB spectra of complexes **6–9** show mass peaks according to the mono-cationic species $[Ag^IL]^+$ (m/z 427 for **6–8** and 551 for **9**).

Crystals suitable for X-ray diffraction studies of **6** and **7** were grown from diffusion of acetone into a solution of **6** in MeOH and from diffusion of MeOH into a solution of **7** in acetonitrile. These two compounds involve the same ligand, but differ in their anions, TsO$^-$ for **6** and PF_6^- for **7**. Although poor quality crystals of complex **6** were grown in a reproducible manner, the connectivity can be deduced unequivocally. Both structures showed dinuclear dimers containing two Ag(I) ions bridged by two NHC ligands. The 2+ charge is balanced by two non-interacting anions. Silver NHC complexes show diverse structures in the solid state, depending on several factors (Ag/L ratio, nature of the NHC ligand, source of silver, counter ions, solvent and temperature). As a matter of fact, addition of a methanolic solution of NH$_4$PF$_6$ to **6**, to afford **7**, dramatically changes the arrangement of the ligands around the silver ions (Figs. 1 and 2). Complex **6** crystallizes in the triclinic space group $P\bar{1}$ with one dicationic dimer and two TsO$^-$ anions in the asymmetric unit. The X-ray structure of **6** (Fig. 1) shows a nearly linear coordination geometry around the silver atoms with silver–carbene bond distances between 2.039(11) Å and 2.104(11) Å and bond angles of 179.0(5)° and 174.9(5)°. Due to the flexibility of this ligand, the two bis-coordinated silver linkages adopt a crossed

Fig. 2. Structure of **7** (50% probability level). H atoms, anions and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Ag(1)–C(1) 2.086(3), Ag(1)–C(18) 2.084(3), Ag(2)–C(9) 2.087(3), Ag(2)–C(26) 2.093(3), Ag(1)···Ag(2) 6.305, C(18)–Ag(1)–C(1) 170.96(13), C(9)–Ag(2)–C(26) 174.29(12).

conformation with dihedral angles C(11)–Ag–Ag–C(1) of 93.86° and C(18)–Ag–Ag–C(28) of 94.53°.

The structure of the "helical" cation results in a weak Ag···Ag interaction (3.074 Å), which is shorter than the sum of the Van der Waals radii (3.40 Å) [23]. Compound **7** crystallizes in the monoclinic space group $P2_1/n$ with the asymmetric unit containing one dicationic dimer, two PF_6^- anions and 3.25 molecules of methanol. Compound **7** forms a "shell-like" structure with the same orientation for all alcohol chains, thus creating a solvent pocket with the OH groups being turned inside (Fig. 2).

The two NHCs units adopt a parallel conformation. Coordination about each Ag(I) slightly deviates from linearity, with classical silver–carbene bonds ranging from 2.084(3) to 2.093(3) Å and C–Ag–C bond angles of 170.93(16)° and 174.29(12)° [24]. This little deviation could arise from the folding up of the molecule imposed by hydrogen interactions between the alcohol groups and methanol molecules.

The complexes form a tube in the crystal, which host the solvent molecules (Fig. 3). This channel like arrangement allows a high liberty for the methanol molecules in solid state, leading to high disorder problems. In both structures, no contact between oxygen atoms of the alcohols and silver ions occurs. Neither complex shows extended intermolecular metal–metal interactions. We were not able to determine
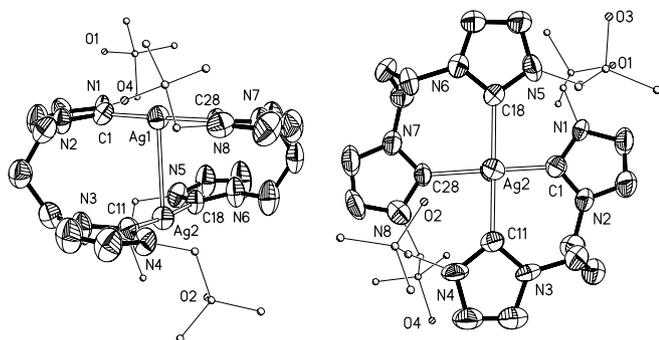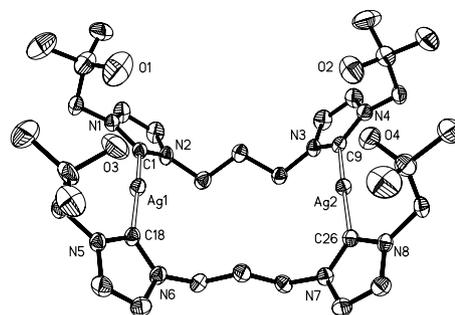

Fig. 1. Structure of **6** (50% probability level). H atoms and anions are omitted and parts of the molecule are simplified for clarity. Crossed conformation is depicted on the right side. Selected bond lengths (Å) and angles (°): Ag(1)–C(1) 2.073(12), Ag(1)–C(28) 2.104(11), Ag(2)–C(11) 2.039(11), Ag(2)–C(18) 2.099(11), Ag(1)–Ag(2) 3.074(2), C(28)–Ag(1)–C(1) 179.0(5), C(11)–Ag(2)–C(18) 174.9(5).
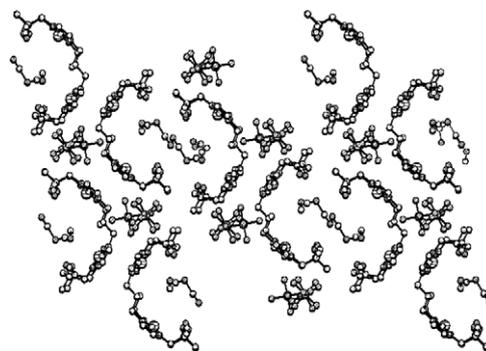

Fig. 3. Crystal packing of **7**.

either anions or solvents employed for crystallisation play an important role for the obtained helical or parallel conformations. Similar structures were precedently obtained for silver(I) complexes of ether-functionalised bis-carbene ligands, by two independent groups [25,26]. The flexibility of this kind of ligands, allowed several conformations which are probably influenced by crystal-packing and intra- and inter-molecular forces.

3. Conclusion

We have prepared alcohol functionalised diimidazolium salts with varied bridging arms and different substituents on the pendant OH arms, using a modulable synthetic strategy. Corresponding silver–carbene complexes $Ag^I(carbene)_2$ have been synthesized. Two dinuclear Ag(I) complexes have been structurally characterised in the presence of non coordinating anions TsO^- and PF_6^-, respectively, showing considerable variations in solid state geometries. We continue to explore these potentially alkoxy-functionalised bis-NHC ligands to design new attractive catalysts.

4. Experimental

4.1. N-functionalised heterocyclic dicarbene silver complexes 6 and 7

4.1.1. Complex 6
A Schlenk was charged with Ag_2O (0.417 mg, 1.8 mmol), **2** (0.600 g, 0.9 mmol), 4 Å MS (1.0 g) and DMSO (15 mL). This mixture was stirred under argon at 50 °C for 14 h, then diluted with dichloromethane (25 mL) and filtered on a celite bed. On addition of diethylether (60 mL), a colorless solid precipitates. After filtration, the desired product was obtained as a colourless solid. Yield: 0.475 g, 88%. Anal. Calc. for $C_{24}H_{35}N_4O_5$-SAg: C, 48.08; H, 5.88; N, 9.35. Found: C, 47.74; H, 5.61; N, 9.15%. ^1H NMR (300 MHz, DMSO-d_6): $\delta = 7.64$ (d, 2H, H_3, $^3J = 1.5$ Hz), 7.51 (bs, 2H, H_4), 7.48 (d, 2H, H_{ArTsO}^-, $^3J = 7.8$ Hz), 7.12 (d, 2H, H_{ArTsO}^-, $^3J = 7.8$ Hz), 4.84 (s, 2H, OH), 4.13 (t, 4H, H_2, $^3J = 5.4$ Hz), 3.73 (s, 4H, H_6), 2.26 (s, 3H, $H_{CH_3TsO}^-$), 1.01 (s, 12H, $H_{8,9}$). ^{13}C NMR (75 MHz, DMSO-d_6): $\delta = 181.3$ (pseudod, 2C, C_5), 146.3 (2C, C_{ArTsO}^-), 138.1 (2C, C_{ArTsO}^-), 128.5 (4C, C_{ArTsO}^-), 125.9 (4C, C_{ArTsO}^-), 124.7 (2C, C_4), 120.9 (2C, C_3), 68.9 (2C, C_7), 54.7 (2C, C_6), 47.8 (2C, C_2), 31.1 (1C, C_1), 27.7 (4C, $C_{8,9}$), 21.2 (2C, $H_{CH_3TsO}^-$)). MS (FAB): $m/z = 427$ $[M-TsO^-]^+$.

4.1.2. Complex 7
Ion exchange of **6** (0.71 g, 0.8 mmol) was realised in a 5 mL methanolic solution of NH_4PF_6 (0.260 mg, 1.60 mmol). After filtration, the colourless solid was obtained. Yield: 0.42 g, 92%. Anal. Calc. for $C_{17}H_{28}N_4O_2P_1F_6Ag$: C, 35.62; H, 4.92; N, 9.77. Found: C, 35.50; H, 4.89; N, 9.44%. ^1H NMR (300 MHz, DMSO-d_6): $\delta = 7.64$ (bs,

2 H, H_3), 7.50 (bs, 2H, H_4), 4.84 (s, 2H, OH), 4.13 (bs, 4H, H_2), 3.73 (s, 4H, H_6), 1.01 (s, 12H, $H_{8,9}$). ^1H NMR (300 MHz, CD$_3$CN): $\delta = 7.31$ (d, 2H, H_3, $^3J = 1.8$ Hz), 7.30 (d, 2H, H_4, $^3J = 1.8$ Hz), 4.19 (t, 4H, H_2, $^3J = 6.0$ Hz), 3.82 (s, 4H, H_6), 3.08 (s, 2H, OH), 2.51 (m, 2H, H_1), 1.11 (s, 12H, $H_{9,8}$). ^{13}C NMR (75 MHz, CD$_3$CN): $\delta = 181.9$ (2C, C_5), 124. 1 (2C, C_4), 120.3 (2C, C_3), 69.4 (2C, C_7), 61.4 (2C, C_6), 48.2 (2C, C_2), 30.6 (1C, C_1), 26.5 (4C, $C_{8,9}$). ^{31}P NMR (121 MHz, DMSO-d_6): $\delta = -144.2$ (septuplet $J_{PF} = 716.8$ Hz). MS (FAB): $m/z = 427$ $[M-PF_6^-]^+$.

4.1.3. Structure determinations
*Crystal data for **6** and **7***. Complex **6**: $C_{48}H_{70}Ag_2N_8O_{10}S$, $M = 1198.98$, triclinic, $P\bar{1}$, $a = 11.686(3)$ Å, $b = 12.574(3)$ Å, $c = 20.967(5)$ Å, $\alpha = 102.935(5)°$, $\beta = 97.087(5)°$, $\gamma = 108.452(5)°$, $V = 2784.9(12)$ Å^3, $Z = 2$, $T = 173(2)$ K. 19 370 reflections (7857 independent, $R_{int} = 0.0280$) were collected. Largest electron density residue: 4.127 e Å^{-3}, R_1 (for $I > 2\sigma(I)$) = 0.0962 and $wR_2 = 0.2424$ (all data) with $R_1 = \sum ||F_o| - |F_c||/\sum |F_o|$ and $wR_2 = (\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2)^{0.5}$. Complex **7**: $C_{37.25}H_{69}Ag_2F_{12}N_8O_{9.75}P_2$, $M = 1250.68$, monoclinic, $P2_1/n$, $a = 15.6227(3)$ Å, $b = 12.4109(2)$ Å, $c = 28.4935(6)$ Å, $\beta = 100.024(1)°$, $V = 5440.32(18)$ Å^3, $Z = 4$, $T = 173(2)$ K. 46 510 reflections (9165 independent, $R_{int} = 0.0426$) were collected. Largest electron density residue: 0.526 e Å^{-3}, R_1 (for $I > 2\sigma(I)$) = 0.0305 and $wR_2 = 0.0748$ (all data).

Data for all structures were collected at low temperature using an oil-coated shock-cooled crystal on a Bruker-AXS APEX2 diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS-97) [27] and all non-hydrogen atoms were refined anisotropically using the least-squares method on F^2 [28].

Appendix A. Supplementary material

CCDC 664306 and 664307 contain the supplementary crystallographic data for compounds **6** and **7**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.11.038.

References

[1] K. Öfele, J. Organomet. Chem. 12 (1968) 42.
[2] H.W. Wanzlick, H.J. Schonher, Angew. Chem., Int. Ed. 7 (1968) 141.
[3] A.J. Arduengo III, R.L. Harlow, M. Kline, J. Am. Chem. Soc. 113 (1991) 361.

[4] D. Bourissou, O. Guerret, F.P. Gabbaï, G. Bertrand, Chem. Rev. 100 (2000) 39.

[5] W.A. Herrmann, Angew. Chem., Int. Ed. 41 (2002) 1290.

[6] A.C. Hillier, G.A. Grasa, M.S. Viciu, H.M. Lee, C. Yang, S.P. Nolan, J. Organomet. Chem. 653 (2002) 69.

[7] E. Peris, R.H. Crabtree, Coord. Chem. Rev. 248 (2004) 2239.

[8] W.A. Herrmann, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, Wiley–VCH, Weinheim, 2000, p. 725.

[9] C. Zhang, J. Huang, M.L. Trudell, S.P. Nolan, J. Org. Chem. 64 (1999) 3804.

[10] A.M. Magill, D.S. McGuinness, K.J. Cavell, G.J.P. Britovsek, V.C. Gibson, A.J.P. White, D.J. Williams, B.W. Skelton, A.H. White, J. Organomet. Chem. 617–618 (2001) 546.

[11] E. Peris, J.A. Loch, J. Mata, R.H. Crabtree, Chem. Commun. (2001) 201.

[12] X. Wang, S. Liu, G.X. Jin, Organometallics 23 (2004) 6002.

[13] D.S. McGuinness, V.C. Gibson, J.W. Steed, Organometallics 23 (2004) 6288.

[14] T.M. Trnka, R.H. Grubbs, Acc. Chem. Res. 34 (2001) 18.

[15] R.H. Grubbs (Ed.), Handbook of Metathesis, Wiley–VCH, Weinheim, 2003.

[16] E. Colacino, J. Martinez, F. Lamarty, Coord. Chem. Rev. 251 (2007) 726.

[17] W.A. Herrmann, L.J. Goossen, C. Köcher, G.R.J. Artus, Angew. Chem., Int. Ed. 35 (1996) 2805.

[18] M. Albrecht, R.H. Crabtree, J. Mata, E. Peris, Chem. Commun. (2002) 32.

[19] P.L. Arnold, M. Rodden, K.M. Davis, A.C. Scarisbrick, J.B. Blake, C. Wilson, Chem. Commun. (2004) 1612.

[20] I.S. Edworthy, M. Rodden, S.A. Mungur, K.M. Davis, A.J. Blake, C. Wilson, M. Schröder, P.L. Arnold, J. Organomet. Chem. 690 (2005) 5710.

[21] A.J. Arduengo III, H.V.R. Dias, J.C. Calabrese, F. Davidson, Organometallics 12 (1993) 3405.

[22] I.J.B. Lin, C.S. Vasam, Chem. Rev. 251 (2007) 642.

[23] J.E. Huheey, E.A. Keiter, R.L. Keiter, Inorganic Chemistry: Principles of Structure and Reactivity, 4th ed., Harper Collins College Publishing, New York, 1993.

[24] J.C. Garrison, W.J. Youngs, Chem. Rev. 105 (2005) 3978.

[25] J.-W. Wang, H.-B. Song, Q.-S. Li, F.-B. Xu, Z.-Z. Zhang, Inorg. Chim. Acta 358 (2005) 3653.

[26] D.J. Nielsen, K.J. Cavell, B.W. Skelton, A.H. White, Organometallics 25 (2006) 4850.

[27] G.M. Sheldrick, Acta Crystallogr., Sect. A 46 (1990) 467.

[28] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, Universität Göttingen, 1997.