A New Synthesis of Functionalized 2,2′-Biimidazoles

Kevin Stippich,[a] Robert Kretschmer,[a] Rainer Beckert,*[a] Helmar Goerls[b]

[a] Institute of Organic and Macromolecular Chemistry, Humboldtstr. 10, 07743 Jena, Germany

[b] Institute of Inorganic and Analytical Chemistry, August-Bebel-Str. 2, 07743 Jena, Germany
Fax +493641948212; E-mail: Rainer.Beckert@uni-jena.de

Received 12 November 2009; revised 15 December 2009

Abstract: A new two-step synthesis of N,N′-disubstituted 2,2′-biimidazoles from bisimidoyl chlorides is reported. The bisimidoyl chlorides react smoothly with (2,2-dimethoxyethyl)amine to give bisamidines that are subsequently cyclized to give the corresponding biimidazoles.

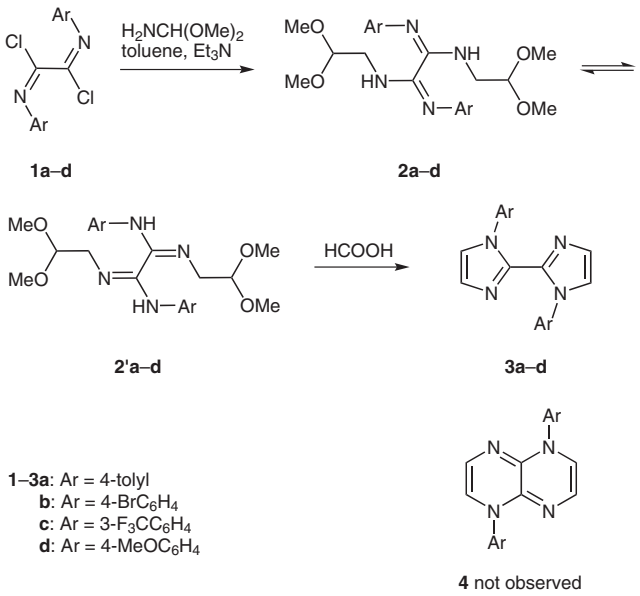
Key words: acetals, biimidazole, heterocycles, cyclization, diazadiene complexes

2,2′-Biimidazoles represent a well-established class of heterocycles and they are of interest as ligands for the formation of metal complexes,[1] as sensors for anions,[2] as building blocks for supramolecular architectures,[3] as sensitizers,[4] and as biologically active derivatives.[5] In addition, bridged derivatives of biimidazole and their benzo analogues have often been used in studies on the formation and dimerization of nucleophilic carbenes.[6]

Starting from glyoxal and its derivatives or from cyanogen, only 2,2′-biimidazoles that are unsubstituted at the nitrogen atoms are accessible,[7] and N-alkylated or N-arylated derivatives are rather rare. The approach most commonly used for generating highly substituted derivatives of 2,2′-biimidazole involves transition metal-mediated homocoupling strategies.[2,3] 2,2′-Biimidazole itself can be transformed (e.g., by N-benzylation) to produce materials that are soluble in organic solvents and can therefore be further functionalized.[8]

Our aim, therefore, was to develop a short and efficient route to derivatives based on C_2 building blocks such as bisimidoyl chlorides **1** derived from oxalic acid. These easily accessible compounds are distinguished by their well-defined electrophilicity, which lies between that of typical acyl chlorides and that of reactive alkyl halides. This permits selective reactions that often initiate cascade reactions. For example, *N*-methylimidazole reacts with bisimidoyl chlorides derived from oxalic acid to give biscationic tricyclic systems, for example diimidazo[1,2-*a*:2′,1′-c]pyrazines.[9] As part of our ongoing studies in the area of multifunctional ligand synthesis, we report our results on the cyclization reactions of bis-electrophilic building blocks **1** with (2,2-dimethoxyethyl)amine.

The products of the reaction of derivatives **1** with nucleophiles are often characterized by their distinct tendency to undergo prototropic rearrangements.[10] Consequently, their aminolysis reaction with amines that possess an additional electrophilic substructure (in this case, aminoacetaldehyde acetals) should lead to functionalized amidines **2**. Upon activation, the latter should be capable of cyclizing intramolecularly via their prototropic form **2′** to finally yield the desired 1,1-bisaryl-2,2′-biimidazoles **3**. Alternatively, a criss-cross cyclization could occur to give the ring-fused products **4**, but this was not observed (Scheme 1).



Scheme 1 Synthesis of amidines **2** and their subsequent cyclization to biimidazoles **3**

The bisimidoyl chlorides **1** were synthesized by using known procedures.[10,11] Aminolysis of compounds **1** was carried out in triethylamine–toluene by heating under reflux to give the bisamidines **2** in yields of up to 70%. This procedure turned out to be easy and fast. Moisture and air were tolerated. Monitoring by thin-layer chromatography showed complete consumption of the starting materials after only 10 minutes or 60 minutes in the case of electron-donor- or electron-acceptor-substituted aryl moieties in **1**, respectively. The bisamidines **2** were obtained as slightly yellow compounds, which are readily soluble in common organic solvents.

Elemental analyses and mass spectral studies confirmed the presence of a 2:1 acylation product **2**. Because these molecules show strong prototropism, the NMR spectra

SYNTHESIS 2010, No. 8, pp 1311–1314
Advanced online publication: 29.01.2010
DOI: 10.1055/s-0029-1218655; Art ID: T21909SS

displayed only broad and poorly resolved signals in chloroform-*d*; the resolution was improved in dimethyl sulfoxide-d_6, which allowed the assignment of the key signals.

On heating in refluxing formic acid for 30 minutes, compounds **2** underwent cyclization in nearly quantitative yields. All the products were fully characterized by means of elemental analyses, mass spectroscopy, and NMR spectroscopy. However, these techniques were unable to distinguish between products **3** and **4**. A single-crystal X-ray analysis of **3b** allowed an unambiguous structural assignment of the structure of this compound, as shown in Figure 1. Therefore, the cyclization products of **2a**–**d** have the structures of the *N*,*N*′-diaryl-2,2′-biimidazoles **3**.

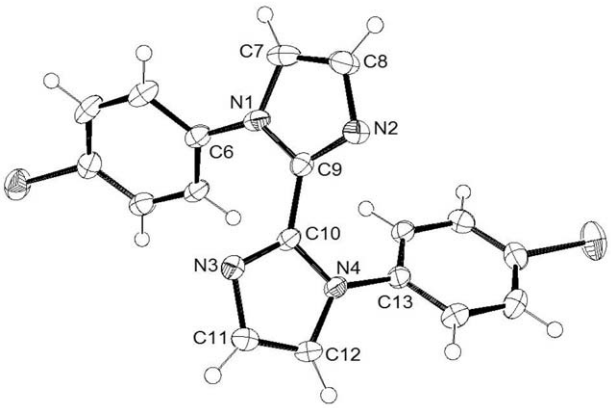


Figure 1 ORTEP plot (50% probability ellipsoids) of the solid-state molecular structure of biimidazole **3b**. Selected bond lengths (Å): N1–C6 1.424(3), N1–C7 1.384(4), N1–C9 1.373(3), N2–C8 1.373(3), N2–C9 1.315(3), C9–C10 1.469(3), N3–C10 1.313(3), N3–C11 1.378(3), N4–C10 1.371(3), N4–C12 1.381(3), N4–C13 1.431(3), C7–C8 1.343(4), C11–C12 1.359(4)

All bond lengths and angles of **3b** were in the expected ranges. The compound may be of considerable interest, since the presence of a bromo substituent should permit further functionalization reactions, e.g. by metal-mediated cross-coupling reactions.

Because 2,2′-biimidazoles are well known to form metal complexes, we attempted the preparation of a molybdenum(0) complex from tetracarbonyl(norbornadiene)molybdenum(0) and the biimidazole **3a** in toluene. Compound **5** was obtained as yellow crystals in 83% yield. The results of an X-ray crystallographic analysis of this complex are shown in Figure 2.

The biimidazole moiety is twisted around the C1a–C1a′-axis by about 20°; this may be due to steric hindrance between the two tolyl substituents. The aromatic rings of these tolyl groups are twisted by about 60° each with respect to the imidazole moiety. The bond lengths of the complex lie in the expected range, and are shown in Figure 2.

To sum up, a series of new 2,2′-biimidazoles **3a–d** were obtained starting from bisimidoyl chlorides **1** by reaction with (2,2-dimethoxyethyl)amine and subsequent cyclization of the bisamidines **2**. The products were obtained easily and rapidly and in good overall yields. The newly synthesized 2,2′-biimidazoles are readily soluble in common organic solvents and, as exemplified by derivative **3b,** have suitable structural features for subsequent cross-coupling by various methods. Whereas the diazadiene subunit in compounds **3** has an s-*trans* arrangement, the complexation reaction with reactive molybdenum carbonyl allowed the synthesis of a typical s-*cis*-diazadiene metal complex **5**.

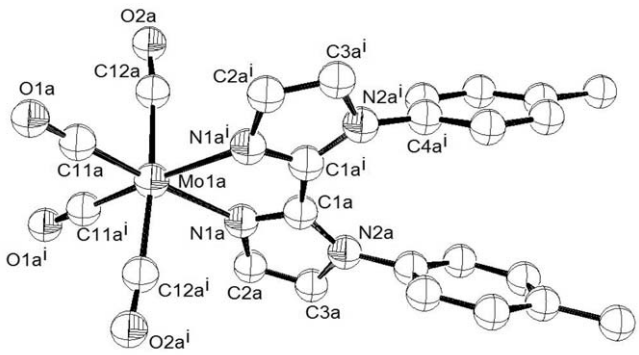


Figure 2 ORTEP plot (50% probability ellipsoids) of the solid-state molecular structure of complex **5**. Selected bond lengths in Å: Mo1a–N1a 2.278(2), Mo1a–N1a^i 2,278(2), N1a–C1a 1.329(4), N1a–C2a 1.372(4), N1a^i–C1a^i 1.329(4), N1a^i–C2a^i 1.374(3), C1a–C1a^i 1.456(5), C1a–N2a 1.353(4), C1a^i–N2a^i 1.355(4), Mo1a–C12a 2.033(3), Mo1a–C11a 1.947(3), Mo1a–C12a^i 2.033(3), Mo1a–C11a^i 1.947(3)

All reagents and solvents were obtained from commercial sources and were used without further purification. Compounds **1a–d** were synthesized according to the methods reported in the literature.[10] The ^{1}H- and ^{13}C NMR-spectra were recorded on a Bruker Avance 250 spectrometer; shifts are given in ppm relative to the signals of the solvent. Melting points were measured on a Krüss KSPS 1000 and are uncorrected. IR spectra were measured on a Bio-Rad FTS-25. Mass spectroscopy was carried out on a Fison Trio 200. Elemental analyses were performed on a Leco CHNS-932. Merck silica gel 60 (0.040–0.063 mm) was used for column chromatography.

Condensation of Biimidoyl Chlorides 1a–d with (2,2-Dimethoxyethyl)amine; General Procedure

Bisimidoyl chloride **1a–d** (3.3 mmol) was dissolved in toluene (25 mL) at r.t. $(MeO)_2CHCH_2NH_2$ (0.69 mL, 6.0 mmol) and Et_3N (1.6 mL, 12 mmol) were added, and the resulting yellow mixture was refluxed for 10–60 min. The soln was cooled to r.t., and the precipitate was filtered off and washed with toluene (10 mL). The filtrates were combined and the solvent was removed in vacuo. The resulting oil or solid was purified by recrystallization or column chromatography.

***N*^{1},*N*^{2}-Bis(2,2-dimethoxyethyl)-*N*′^{1},*N*′^{2}-bis(4-methylphenyl)ethanediimidamide (2a)**

Reaction time: 1 h. The resulting orange oil was crystallized (heptane) to give a colorless solid; yield: 47%; mp 98.5–99.2 °C.

IR (ATR): 3310, 2892, 1634, 1487, 1257, 1125, 1041, 881, 787 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.17 (s, 6 H, CH_3), 3.24 (s, 12 H, OCH_3), 3.60 (br s, 4 H, CH_2), 4.27 (br s, 2 H, CH), 6.39–6.96 (br s, 8 H, aryl-H).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 20.5, 45.2, 53.8, 101.9, 121.3, 128.8, 132.1, 145.5, 151.3.

MS (EI): *m/z* (%) = 443 (100), 442 (86), 367 (41), 189 (52), 131 (57), 75 (64).

Anal. Calcd for $C_{24}H_{34}N_4O_4$: C, 65.14; H, 7.74; N, 12.66. Found: C, 65.19; H, 7.83; N, 12.64.

N'^1,N'^2-Bis(4-bromophenyl)-N^1,N^2-bis(2,2-dimethoxyethyl)ethanediimidamide (2b)

Reaction time: 10 min. The resulting solid was crystallized (*t*-BuOMe) to give a colorless solid; yield: 62%; mp 104.8 °C.

IR (ATR): 3288, 2936, 1613, 1481, 1193, 1118, 1050, 829, 814 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.34 (s, 12 H, OCH_3), 3.40 (br s, 4 H, CH_2), 4.37 (br s, 2 H, CH), 6.39–7.32 (br s, 8 H, aryl-H).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 42.5, 54.2, 101.9, 115.7, 123.2, 131.4, 147.6, 150.2.

MS (EI): *m/z* (%) = 572 (15), 497 (14), 255 (15), 197 (13), 171 (20), 75 (100)

Anal. Calcd for $C_{22}H_{28}Br_2N_4O_4$: C, 46.17; H, 4.93; N, 9.79; Br, 27.92. Found: C, 46.13; H, 4.94; N, 9.51; Br, 27.71.

N^1,N^2-Bis(2,2-dimethoxyethyl)-N'^1,N'^2-bis[3-(trifluoromethyl)phenyl]ethanediimidamide (2c)

Reaction time: 10 min. The resulting orange-brown oil was purified by column chromatography [silica gel, heptane–EtOAc (2:1)]; yield: 60%; colorless solid; mp 84.6–87.0 °C.

IR (ATR): 3380, 2933, 1641, 1523, 1329, 1113, 1069, 797, 699 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.42 (s, 12 H, OCH_3), 3.52 (br s, 4 H, CH_2), 4.49 (br s, 2 H, CH), 6.54–7.39 (br s, 8 H, aryl-H).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 42.4, 54.3, 101.9, 118.3, 119.3, 124.1, 124.7, 128.8, 130.7, 148.7, 150.3.

MS (EI): *m/z* (%) = 551 (19), 550 (23), 443 (16), 243 (22), 145 (12), 75 (100).

Anal Calcd for $C_{24}H_{28}F_6N_4O_4$: C, 52.36; H, 5.13; N, 10.18. Found: C, 52.79; H, 4.87; N, 9.94.

N^1,N^2-Bis(2,2-dimethoxyethyl)-N'^1,N'^2-bis(4-methoxyphenyl)ethanediimidamide (2d)

Reaction time: 1 h. The resulting brown oil was purified by column chromatography [silica gel, CH_2Cl_2–MeOH (95:5)] to give a brown syrup; yield: 16%.

IR (ATR): 3369, 2936, 1610, 1498, 1235, 1124, 1068, 1031, 826 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.32 (s, 12 H, OCH_3) 3.41 (br s, 4 H, CH_2), 3.76 (s, 6 H, Ar-OCH_3), 4.34 (br s, 2 H, CH), 6.61–7.00 (br s, 8 H, aryl-H).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 42.5, 54.0, 55.5, 102.1, 113.9, 122.3, 142.0, 150.6, 155.6.

MS (EI): *m/z* (%) = 475 (58), 474 (100), 399 (57), 306 (35), 205 (62), 147 (100).

Anal. Calcd for $C_{24}H_{34}N_4O_6$: C, 60.74; H, 7.22; N, 11.81. Found: C, 60.73; H, 7.23; N, 11.70.

Cyclization to 2,2′-Biimidazoles 3a–d; General Procedure

A bisamidine **2a–d** (1.0 mmol) was refluxed in HCO_2H (5 mL) for 30 min, and then cooled to r.t. The soln was poured into ice–water, and neutralized with concd aq NH_3. The resulting precipitate was filtered off, washed with H_2O, and dried.

1,1′-Bis(4-methylphenyl)-1*H*,1′*H*-2,2′-biimidazole (3a)

Beige solid; yield: 67%; mp 132.7–133.0 °C.

IR (ATR): 1513, 1417, 1303, 1080, 963, 819, 741, 724 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.31 (s, 6 H, Aryl-CH_3), 6.68 (d, *J* = 8.3 Hz, 4 H, aryl-H), 6.98 (d, *J* = 8.3 Hz, 4 H, aryl-H), 7.03 (d, *J* = 1.0 Hz, 2 H, imidazole-H), 7.21 (d, *J* = 1.0 Hz, 2 H, imidazole-H).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 21.0, 121.3, 124.0, 129.5, 129.6, 134.7, 137.4, 137.6.

MS (EI): *m/z* (%) = 315 (18), 314 (66), 313 (100), 223 (16), 91 (11).

Anal Calcd for $C_{20}H_{18}N_4$: C, 76.41; H, 5.77; N, 17.82. Found: C, 75.97; H, 5.62; N, 17.79.

1,1′-Bis(4-bromophenyl)-1*H*,1′*H*-2,2′-biimidazole (3b)

From bisamidine **2b** (2.0 mmol) in HCO_2H (5 mL); beige solid; yield: 90%; mp 203.2–203.6 °C.

IR (ATR): 1487, 1424, 1300, 1065, 960, 830, 738, 717 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.71 (d, *J* = 8.8 Hz, 4 H, aryl-H), 7.06 (d, *J* = 1.3 Hz, 2 H, imidazole-H), 7.25 (d, *J* = 1.3 Hz, 2 H, imidazole-H), 7.36 (d, *J* = 8.8 Hz, 4 H, aryl-H).

^{13}C NMR (63 Hz, $CDCl_3$): δ = 121.3, 121.6, 125.8, 130.2, 132.3, 136.1, 137.1.

MS (EI): *m/z* (%) = 445 (62), 444 (66), 443 (100), 287 (18), 181 (34), 155 (22).

Anal. Calcd for $C_{18}H_{12}Br_2N_4$: C, 48.68; H, 2.72; N, 12.62; Br, 35.98. Found: C, 48.38; H, 2.85; N, 12.26; Br, 36.42.

1,1′-Bis[(3-trifluoromethyl)phenyl]-1*H*,1′*H*-2,2′-biimidazole (3c)

Beige solid; yield: 96%; mp 206.7–207.7 °C.

IR (ATR): 102, 1496, 1473, 1461, 1326, 1289, 1166, 1115, 1066, 980, 893, 783, 629 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.97–7.02 (m, 4 H, aryl-H), 7.13 (d, *J* = 1.1 Hz, 2 H, imidazole–H), 7.32 (d, *J* = 1.1 Hz, 2 H, imidazole-H), 7.35 (d, J = 8.0 Hz, 2 H, aryl-H), 7.51 (d, J = 8.0 Hz, 2 H, aryl-H).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 120.8, 121.1, 124.4, 125.2, 127.1, 129.9, 130.7, 131.2, 137.0, 137.4.

MS (EI): *m/z* (%) = 423 (44), 422 (100), 421 (86), 277 (31), 262 (22), 145 (22).

Anal. Calcd for $C_{20}H_{12}F_6N_4$: C, 56.88; H, 2.86; N, 13.27. Found: C, 57.12; H, 2.95; N, 13.56.

1,1′-Bis(4-methoxyphenyl)-1*H*,1′*H*-2,2′-biimidazole (3d)

From bisamidine **2d** (0.67 mmol) in HCO_2H (3 mL); beige solid; yield: 82%; mp 190.5–190.9 °C (dec).

IR (ATR): 1514, 1466, 1300, 1251, 1188, 1108, 1026, 853, 747, 710 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.77 (s, 6 H, OCH_3), 6.71 (m, 8 H, aryl-H), 7.01 (d, *J* = 1.0 Hz, 2 H, imidazole-H), 7.21 (d, *J* = 1.0 Hz, 2 H, imidazole-H).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 55.5, 114.1, 121.5, 125.4, 129.5, 130.3, 137.7, 158.8.

MS (EI): *m/z* (%) = 346 (56), 345 (100), 239 (16), 224 (12), 173 (10), 77 (6).

Anal. Calcd for $C_{20}H_{18}N_4O_2$: C, 69.35; H, 5.24; N, 16.17. Found: C, 68.98; H, 5.37; N, 16.23.

1,1′-Bis(4-bromophenyl)-1*H*,1′*H*-2,2′-biimidazole(tetracarbonyl)molybdenum(0) (5)

Biimidazole **3b** (78 mg, 0.25 mmol) was suspended in toluene (10 mL), and tetracarbonyl(norbornadiene)molybdenum(0) (75 mg, 0.25 mmol) was added. The yellow suspension was heated to 60 °C for 2 h, then refluxed for 2 h. The soln became brown and a yellow precipitate was formed. The mixture was cooled to r.t and filtered, and the residue was collected and dried. Single crystals of complex **5** were obtained by heating to reflux in THF and then slowly cooling to r.t. to give a yellow solid; yield: 83%.

IR (ATR): 3159, 3136, 2010, 1877, 1858, 1816, 1802, 1513, 1428, 820, 748 cm^{-1}.

^1H NMR (250 MHz, CD_3CN): δ = 2.29 (s, 6 H, CH_3), 6.76 (d, *J* = 8.3 Hz, 4 H, aryl-H), 7.06 (d, *J* = 8.3 Hz, 4 H, aryl-H), 7.12 (s, 2 H, imidazole-H), 7.29 (s, 2 H, imidazole-H)

^{13}C NMR (63 MHz, CD_3CN): δ = 21.0, 123.1, 125.0, 129.6, 130.7, 133.6, 135.4, 138.7

MS (EI): *m/z* (%) = 313 (100), 223 (8), 91 (4), 28 (15)

MS (ESI): *m/z* (%) = 651 (87), 337 (100), 315 (26)

Crystal Structure Determination

The intensity data for the compound were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects, but not for absorption effects.[12,13] The structure was solved by direct methods (SHELXS),[14] and refined by full-matrix least-squares techniques against Fo^2 (SHELXL-97).[15] All hydrogen atoms were included at calculated positions with fixed thermal parameters. All nonhydrogen atoms were refined anisotropically.[15] XP (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal Data for **3b**:[16] $C_{18}H_{12}Br_2N_4$, Mr = 444.14 g·mol^{-1}, light brown prism, size 0.05 × 0.05 × 0.04 mm^3, triclinic, space group *Pi*, *a* = 8.6364(4), *b* = 9.1538(3), *c* = 10.9804(4) Å, α = 84.110(2), β = 78.949(2), γ = 77.527(2)°, *V* = 830.16(6) $Å^3$, *T* = –90 °C, *Z* = 2, $\rho_{calcd.}$ = 1.777 g·cm^{-3}, μ (Mo-K_α) = 48.89 cm^{-1}, *F*(000) = 4,365,774 reflections in *h*(–11/10), *k*(–11/11), *l*(–14/14), measured in the range 1.89° ≤ θ ≤ 27.49°, completeness θ_{max} = 99.3%, 3773 independent reflections, R_{int} = 0.0231, 2950 reflections with $F_o > 4\sigma(F_o)$, 218 parameters, 0 restraints, $R1_{obs}$ = 0.0346, wR^2_{obs} = 0.0775, $R1_{all}$ = 0.0519, wR^2_{all} = 0.0841, GOOF = 1.015, largest difference peak and hole: 0.371/–0.688 e $Å^{-3}$.

Crystal Data for **5**:[16] $C_{24}H_{18}MoN_4O_4$, Mr = 522.36 g·mol^{-1}, yellow prism, size 0.05 × 0.05 × 0.04 mm^3, monoclinic, space group *P2*/c, *a* = 12.9060(5), *b* = 13.1590(6), *c* = 15.8520(5) Å, β = 122.520(3)°, *V* = 2270.03(15) $Å^3$, *T* = –90 °C, *Z* = 4, $\rho_{calcd.}$ = 1.528 g·cm^{-3}, μ (Mo-K_α) = 6.16 cm^{-1}, *F*(000) = 1056, 22201 reflections in *h*(–16/16), *k*(–15/17), *l*(–20/18), measured in the range 1.87° ≤ θ ≤ 27.48°, completeness θ_{max} = 99.9%, 5193 independent reflections, R_{int} = 0.1108, 3316 reflections with $F_o > 4\sigma(F_o)$, 301 parameters, 0 restraints, $R1_{obs}$ = 0.0425, wR^2_{obs} = 0.0807, $R1_{all}$ = 0.0957, wR^2_{all} = 0.0935, GOOF = 0.981, largest difference peak and hole: 0.640/–0.981 e $Å^{-3}$.

Acknowledgment

R.K. thanks the Hans-Böckler-Stiftung for a scholarship.

References

(1) (a) Tadokoro, M.; Isobe, K.; Uekusa, H.; Ohashi, Y.; Toyoda, J.; Tashiro, K.; Nakasuji, K. *Angew. Chem.* **1999**, *111*, 102. (b) Goulle, V.; Thummel, R. P. *Inorg. Chem.* **1990**, *29*, 1767.
(2) Causey, C. P.; Allen, W. E. *J. Org. Chem.* **2002**, *67*, 5963.
(3) Allen, W. E.; Fowler, C. J.; Lynch, V. M.; Sessler, J. L. *Chem. Eur. J.* **2001**, 7,; 721.
(4) Nonell, S.; Borrell, J. I.; Borros, S.; Colominas, C.; Rey, O.; Rubio, N.; Sanchez-Garcia, D.; Teixido, J. *Eur. J. Org. Chem.* **2003**, 1635.
(5) Melloni, P.; Fusar-Bassini, D.; Logemann, W.; Forgiane, A.; Dradi, E.; DeCarneri, I.; Bianchi, A.; Trane, F. *Eur. J. Med. Chem.* **1975**, *10*, 514.
(6) (a) Shi, Z.; Thummel, R. P. *Tetrahedron Lett.* **1995**, *36*, 2741. (b) Thummel, R. P.; Goulle, V.; Chen, B. *J. Org. Chem.* **1989**, *54*, 3057. (c) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G. R. *Chem. Eur. J.* **1996**, *2*, 772. (d) Taton, T. A.; Chen, P. *Angew. Chem.* **1996**, *108*, 1098. (e) Ames, J. R.; Houghtaling, M. A.; Terrian, D. L.; Mitchell, T. P. *Can. J. Chem.* **1997**, *75*, 28.
(7) (a) Kuhn, R.; Blau, W. *Liebigs Ann. Chem.* **1957**, *605*, 32. (b) Fieselmann, B.; Hendrickson, D. *Inorg. Chem.* **1978**, *17*, 2078. (c) Nurgatin, V. V.; Ginzburg, B. M.; Sharnin, G. B.; Polyanskii, V. F. *Khim. Geterotsikl. Soedin.* **1987**, *8*, 1069; *Chem. Abstr.* **1988**, *109*, 37778e. (d) Duranti, E.; Balsamini, C. *Synthesis* **1974**, 815. (e) Matthews, D. P.; Whitten, J. P.; McCarthy, J. R. *Synthesis* **1986**, 336.
(8) (a) Sanchez-Garcia, D.; Borros, S.; Nonell, S.; Borrell, J. I.; Colominas, C.; Teixido, J. *J. Heterocycl. Chem.* **2002**, *39*, 733. (b) Whitten, J. P.; Matthews, D. P.; McCarthy, J. R.; Barbuch, R. J. *J. Heterocycl. Chem.* **1988**, *25*, 1845.
(9) Welzel, T.; Beckert, R.; Fischer, R.; Rau, S.; Walther, D.; Görls, H. *Tetrahedron* **2006**, *62*, 731.
(10) Buehrdel, G.; Beckert, R.; Petrlikova, E.; Herzigova, P.; Klimesova, V.; Fleischhauer, J.; Goerls, H. *Synthesis* **2008**, 3071.
(11) Lindauer, D.; Beckert, R.; Görls, H.; Fehling, P.; Döring, M. *J. Prakt. Chem./Chem.-Ztg.* **1995**, *337*, 143.
(12) *COLLECT, Data Collection Software*, Nonius BV: Delft, **1998**.
(13) Otwinowski, Z.; Minor, W. In *Methods in Enzymology*, Vol. 276; Carter, C. W.; Sweet, R. M., Eds.; Academic Press: San Diego, **1997**, 307.
(14) Sheldrick G. M.; *Acta Crystallogr., Sect. A*; **1990**, *46*: 467.
(15) Sheldrick, G. M. *SHELX97 [Includes SHELXS97, SHELXL97 and CIFTAB]: Programs for Crystal Structure Analysis (Release 97-2)*; Institut für Anorganische Chemie der Universität: Göttingen (Germany), **1998**.
(16) Crystallographic data for compounds **3b** and **5** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-752317 and CCDC-752318, respectively; copies can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(1223)336033 or email: deposit@ccdc.cam.ac. uk].