Template synthesis of tungsten complexes with saturated N-heterocyclic carbene ligands†

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Tungsten complex 5 with a coordinated 2-azidoethyl isocyanide ligand reacts with PMe_3 at the azido function to give a complex with a coordinated iminophosphorane which upon hydrolysis of the P=N bond yields a complex with an NH,NH-stabilized N-heterocyclic carbene ligand, 7; alkylation of the carbene ring nitrogen atoms gives a complex with an *N*,*N*′-dialkylated imidazolidin-2-ylidene ligand, 8.

Nucleophilic attack at the carbon atom of a coordinated isocyanide is one of the oldest methods for the preparation of carbene complexes.[1] Particularly protic nucleophiles like alcohols and primary amines have been useful in this reaction.[2] The use of functionalized isocyanides containing both the isocyanide function and the nucleophile in the same molecule gives access to complexes with heterocyclic carbene ligands through an intramolecular 1,2-addition across the CN triple bond.

We have reported on the template controlled cyclization of 2-hydroxyphenyl isocyanide which was obtained from complexes containing 2-(trimethylsiloxy)phenyl isocyanide *via* O–Si bond cleavage.[2] The synthesis of complexes containing benzannulated NH,NH-stabilized N-heterocyclic carbene ligands was also achieved in a template synthesis.[3] This method constitutes an alternative approach for the preparation of carbene complexes compared to the direct reaction of stable benzannulated carbene ligands[4] or benzimidazolium salts[5] with transition metal complexes. Here we report on the cyclization reaction of coordinated 2-azidoethyl isocyanide **4** which allows the template synthesis of complexes with the widely used saturated imidazolidin-2-ylidenes.[6]

2-Azidoethyl isocyanide **4** was synthesized by reaction of 2-bromoethylamine hydrobromide with sodium azide in water followed by formylation of the primary amine and dehydration of the obtained formamide using the method of Ugi or Casanova[7] (Scheme 1). The isocyanide and the azido function in **4** were identified by their absorptions in the IR spectrum at $\nu = 2152\ cm^{-1}$ and $\nu = 2109\ cm^{-1}$, respectively.‡ In the $^{13}C\{^1H\}$ NMR spectrum the resonances for the isocyanide carbon atom (δ 160.3 ppm) and for the carbon atom of the adjacent methylene group (δ 41.2 ppm) are observed as triplets due to $^1J(^{13}C–^{14}N)$ coupling typical of uncoordinated isocyanides.[8]

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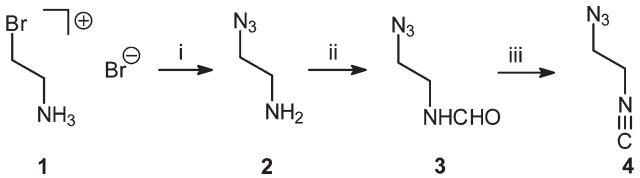
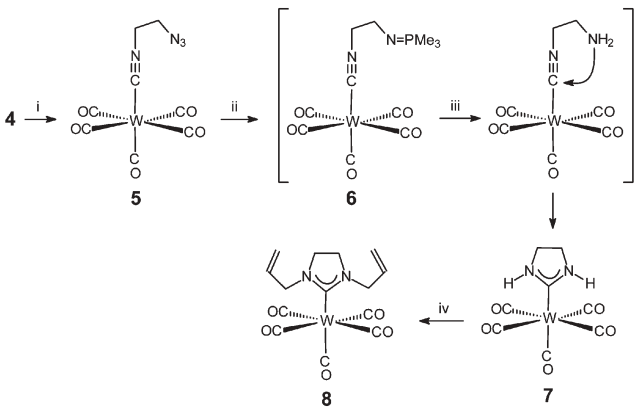
Ligand **4** coordinates to photochemically generated $[W(CO)_5(THF)]$ to give the isocyanide complex **5**‡ (Scheme 2). Complex **5** was identified by NMR and by IR spectroscopy which showed the absorption for the CN stretching mode at $\nu = 2187\ cm^{-1}$. The isocyanide ligand in **5** reacts at the azido function with trimethylphosphine in a Staudinger-type[9] reaction to give the trimethylphosphorane complex **6**, which was not isolated. Hydrolysis of the trimethylphosphorane under acidic conditions with traces of water in protic solvents (methanol) affords a complex with the 2-aminoethyl isocyanide ligand which is not stable and immediately undergoes an intramolecular cyclization to give a complex with the NH,NH-stabilized carbene ligand **7**‡ (Scheme 2).

The formation of the carbene complex **7** was confirmed by the observation of the resonance for the carbene carbon atom in the ^{13}C NMR spectrum at δ 202.2 ppm and by the lack of absorptions for the N≡C and N_3 groups in the IR spectrum. The IR spectrum



Scheme 1 *Reagents and conditions*: (i) NaN_3 (excess), H_2O, 70 °C, 5 h; (ii) $CH_3C(O)OCHO$, THF, 25 °C, 5 h; (iii) *p*Tol-SO_2Cl, solvent C_9H_7N, 25 °C.



Scheme 2 *Reagents and conditions*: (i) $[W(CO)_5(THF)]$, THF, 25 °C, 12 h; (ii) PMe_3, $-\ N_2$; (iii) H_2O, HCl (catalytic amount), MeOH, 25 °C, 5 h; (iv) 1. KO*t*Bu, DMF, 25 °C, 2 h, 2. $CH_2CHCH_2–Br$, DMF, 25 °C, 5 h (for mono *N*-alkylation, repeat (iv) for second *N*-alkylation).

of **7** shows, however, a strong new absorption for the N–H stretching mode. Fehlhammer *et al.* showed that 2-hydroxyethyl isocyanide coordinated to the $W(CO)_5$ complex fragment does not cyclize to the NH,O-stabilized carbene ligand which we attribute to the lower nucleophilicity of the hydroxyl group.[10] However, both 2-aminophenyl isocyanide[2,3] and 2-hydroxyphenyl isocyanide[2,11] readily cyclize to give ylidenes when coordinated to the $W(CO)_5$ complex fragment.

The acidity of the NH protons in complex **7** allows the synthesis of a complex with an *N*-alkyl functionalized carbene ligand. Stepwise or simultaneous deprotonation of **7** and subsequent reaction with allyl bromide gives complex **8**‡ with an *N*,*N*′-diallylimidazolidin-2-ylidene ligand (Scheme 2). The ^{13}C NMR spectrum of complex **8** exhibits a resonance for the carbene carbon atom at δ 207.7 ppm, slightly downfield compared to this resonance in the complex with the NH,NH-substituted carbene ligand **7**.

The molecular structures of **7** and **8** were determined by X-ray diffraction (Fig. 1).§ The structure analyses confirmed the formation of the carbene complexes. The W–C1 separation in **7** (2.221(5) Å) compares well to the equivalent distance in the complex with an NH,NH-stabilized benzimidazolin-2-ylidene ligand (2.203(4) Å).[3a] A significant lengthening of the W–C distance is observed upon *N*,*N*′-alkylation for both the *N*,*N*′-diallylimidazolidin-2-ylidene (2.266(3) Å in **8**) and the *N*,*N*′-diallylbenzimidazolin-2-ylidene (2.256(3) Å) ligand.[3a] These distances fall in the range observed for the $W(CO)_5$ complex with the unsaturated *N*,*N*′-diethylimidazolin-2-ylidene (2.275(8) Å).[12] A significantly shorter W–C(carbene) separation was observed for the $W(CO)_5$ complex with the benzoxazolin-2-ylidene ligand (2.198(5) Å).[11]

Here we have described an alternative route leading to complexes with N-heterocyclic carbene ligands of the imidazolidin-2-ylidene type. Previously such complexes were obtained by cleavage of electron rich enetetramines or from imidazolidinium salts by reaction with suitable transition metal precursors. In contrast to this, we present a method to generate the N-heterocyclic carbene ligand at a suitable template metal center starting from a coordinated β-functionalized alkyl isocyanide. This method offers some advantages. For example, it gives access to complex **7** with an NH,NH-stabilized imidazolidinylidene, a ligand not stable or available in the free state. Alkylation of the NH-functions of the carbene ligand in **7** generates an N-heterocyclic carbene ligand of the imidazolidin-2-ylidene type. The method described here could, for example, lead to new Grubbs-type catalysts by *generating* the carbene ligand from an isocyanide at Ru(II) instead of *substituting* a ligand at Ru(II) for an N-heterocyclic carbene ligand.

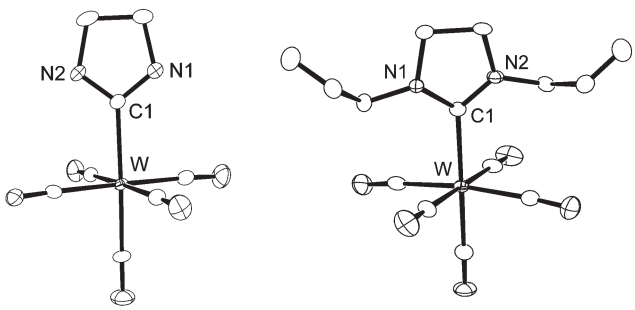


Fig. 1 Thermal ellipsoid plots showing the molecular structures of complexes **7** (left) and **8** (right). Hydrogen atoms have been omitted for clarity. Selected bond distances [Å] and bond angles [°] for **7** [**8**]: W–C1 2.221(5) [2.266(3)], C1–N1 1.326(6) [1.362(4)], C1–N2 1.330(6) [1.349(4)]; N1–C1–N2 106.6(4) [106.8(2)].

Notes and references

‡ **Spectroscopic data for compounds 4–8**. **4**: ^1H NMR (300 MHz, THF-d_8): δ 3.60 (m, 4H, CH_2); $^{13}C\{^1H\}$ NMR (75.4 MHz, THF-d_8): δ 160.3 (t, $^1J_{CN}$ = 4.5 Hz, CN), 50.0 (CH_2–N_3), 41.2 (t, $^1J_{CN}$ = 7.0 Hz, CH_2–NC); IR (benzene): ν 2152 (s, CN), 2109 (s, N_3). **5**: ^1H NMR (300 MHz, $CDCl_3$): δ 3.89 (t, $^3J_{HH}$ = 6 Hz, 2H, CH_2–N_3), 3.65 (t, $^3J_{HH}$ = 6 Hz, 2H, CH_2–CN); $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 196.3 (CO_{trans}), 194.4 (CO_{cis}), 147.3 (*C*N–CH_2), 50.0 (CH_2–N_3), 44.3 (*C*H_2–NC); IR (KBr): ν 2187 (s, CN), 2104 (s, N_3), 2069 (s, CO), 1923 (s, br, CO); MS (EI): *m*/*z* 420 (22, $[M]^+$), 392 (5, $[M - CO]^+$), 364 (2, $[M - 2CO]^+$), 336 (18, $[M - 3CO]^+$), 308 (31, $[M - 4CO]^+$), 280 (54, $[M - 5CO]^+$). **7**: ^1H NMR (400 MHz, THF-d_6): δ 7.53 (s, 2H, NH), 3.32 (s, 4H, CH_2); $^{13}C\{^1H\}$ NMR (75.4 MHz, THF-d_6): δ 202.2 (NCN), 200.4 (CO_{trans}), 198.8 (CO_{cis}), 45.0 (CH_2); IR (KBr): ν 3475 (s, NH), 2063 (s, CO), 1888 (s, CO); MS (EI): *m*/*z* 394 (70, $[M]^+$), 366 (36, $[M - CO]^+$), 338 (24, $[M - 2CO]^+$), 310 (100, $[M - 3CO]^+$), 282 (91, $[M - 4CO]^+$), 254 (60, $[M - 5CO]^+$). **8**: ^1H NMR (400 MHz, THF-d_6): δ 5.81 (ddt, 2H, $^3J_{HH}$ = 16, 10, 4 Hz, CH_2–*CH*=CH_2), 5.24–5.21 (m, 4H, CH_2–CH=*CH*$_2$), 4.36 (m, 4H, *CH*$_2$–CH=CH_2), 3.51 (s, 4H, N–CH_2–CH_2–N); $^{13}C\{^1H\}$ NMR (100.6 MHz, THF-d_8): δ 207.7 (NCN), 201.6 (CO_{trans}), 198.9 (CO_{cis}), 134.5 (CH_2–*C*H=CH_2), 118.9 (CH_2–CH=*C*H_2), 56.5 (N–*C*H_2–CH), 49.0 (N–CH_2–CH_2–N); MS (EI): *m*/*z* 474 (26, $[M]^+$), 446 (18, $[M - CO]^+$), 390 (23, $[M - 3CO]^+$), 362 (100, $[M - 4CO]^+$).

§ **Crystal data for compounds 7 and 8**. **7**: $C_8H_6N_2O_5W$, M = 394.00, T = 153(2) K, λ = 0.71073 Å, triclinic, *P*-1, Z = 2, a = 6.6670(10), b = 8.5579(12), c = 10.1724(15) Å, α = 94.486(3), β = 106.524(3), γ = 100.679(3)°, V = 541.48(14) Å^3, 6155 measured reflections, 3109 unique reflections (R_{int} = 0.0370), R = 0.0304, wR = 0.0741 for 2977 contributing reflections [$I \geqslant 2\sigma(I)$], refinement against $|F^2|$ with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms on calculated positions. **8**: $C_{14}H_{14}N_2O_5W$, M = 474.12, T = 153(2) K, λ = 0.71073 Å, monoclinic, $P2_1/n$, Z = 4, a = 11.181(5), b = 10.629(5), c = 13.731(6) Å, β = 105.519(8)°, V = 1572.3(12) Å^3, 17607 measured reflections, 4579 unique reflections (R_{int} = 0.0473), R = 0.0262, wR = 0.0606 for 4084 contributing reflections [$I \geqslant 2\sigma(I)$], refinement against $|F^2|$ with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms on calculated positions. CCDC 280981 (**7**) and 280982 (**8**). See http://dx.doi.org/10.1039/b510996e for crystallographic data in CIF or other electronic format.

1 (*a*) L. Tschugajeff, M. Skanawy-Grigorjewa and A. Posnjak, *Z. Anorg. Allg. Chem.*, 1925, **148**, 37; (*b*) W. M. Butler, J. H. Enemark, J. Parks and A. L. Balch, *Inorg. Chem.*, 1973, **12**, 451.

2 M. Tamm and F. E. Hahn, *Coord. Chem. Rev.*, 1999, **182**, 175.

3 (*a*) F. E. Hahn, V. Langenhahn, N. Meier, T. Lügger and W. P. Fehlhammer, *Chem.–Eur. J.*, 2003, **9**, 704; (*b*) F. E. Hahn, C. Garcia Plumed, M. Münder and T. Lügger, *Chem.–Eur. J.*, 2004, **10**, 6285; (*c*) F. E. Hahn, V. Langenhahn, T. Lügger, T. Pape and D. Le Van, *Angew. Chem., Int. Ed.*, 2005, **44**, 3759; (*d*) M. Basato, F. Benetollo, G. Faccin, R. A. Michelin, M. Mozzon, S. Pugliese, P. Sgarbossa, S. M. Sbovata and A. Tassan, *J. Organomet. Chem.*, 2004, **689**, 454.

4 (*a*) F. E. Hahn, L. Wittenbecher, R. Boese and D. Bläser, *Chem.–Eur. J.*, 1999, **5**, 1931; (*b*) F. E. Hahn, L. Wittenbecher, D. Le Van and R. Fröhlich, *Angew. Chem., Int. Ed.*, 2000, **39**, 541; (*c*) F. E. Hahn, T. von Fehren and R. Fröhlich, *Z. Naturforsch., B: Chem. Sci.*, 2004, **59**, 1051.

5 (*a*) F. E. Hahn and M. Foth, *J. Organomet. Chem.*, 1999, **585**, 241; (*b*) F. E. Hahn, C. Holtgrewe and T. Pape, *Z. Naturforsch., B: Chem. Sci.*, 2004, **59**, 348.

6 (*a*) T. M. Trnka and R. H. Grubbs, *Acc. Chem. Res.*, 2001, **34**, 18; (*b*) W. H. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1290.

7 (*a*) I. Ugi, U. Fetzer, U. Eholzer, H. Knupfer and K. Offermann, *Angew. Chem., Int. Ed. Engl.*, 1965, **4**, 492; (*b*) J. Casanova, R. E. Schuster and N. D. Werner, *J. Chem. Soc.*, 1963, 4280.

8 (*a*) I. Morishima, A. Mizuno and T. Yonezawa, *J. Chem. Soc. D*, 1970, 1321; (*b*) F. E. Hahn and M. Tamm, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 203; (*c*) F. E. Hahn and M. Tamm, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1212.
9 H. Staudinger and J. Meyer, *Helv. Chim. Acta*, 1919, **2**, 635.
10 (*a*) W. P. Fehlhammer, K. Bartel, B. Weinberger and U. Plaia, *Chem. Ber.*, 1985, **118**, 2220; (*b*) W. P. Fehlhammer, K. Bartel, U. Plaia, A. Völkl and A. T. Liu, *Chem. Ber.*, 1985, **118**, 2235.
11 F. E. Hahn and M. Tamm, *J. Organomet. Chem.*, 1993, **456**, C11.
12 N. Kuhn, T. Kratz, R. Boese and D. Bläser, *J. Organomet. Chem.*, 1994, **470**, C8.

