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CO_2 Binding

An Isolated CO_2 Adduct of a Nitrogen Base: Crystal and Electronic Structures**

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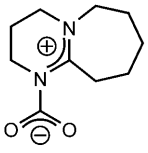
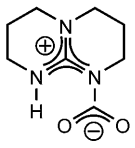
Reversible fixation of carbon dioxide, considered as a cheap and green C1 feedstock, and its facile transformation into valuable raw and fine materials is one of the most exciting challenges and important priorities for the scientific community.[1] The activation of the thermodynamically and kinetically stable CO_2 molecule has been achieved using metal-containing catalysts, while organic bases are also capable of promoting reactions with CO_2. The R_2NH/CO_2 system, which is relevant to industrial processes, has attracted much attention since the beginning of the last century. Hindered amidines and guanidines were found to be particularly efficient catalysts in the synthesis of organic carbonates and urethanes from the respective reactions of alcohols and amines with CO_2, thus avoiding the use of the highly toxic phosgene and its derivatives.[2–5] These nitrogen bases also proved to be useful for the coupling of CO_2 and epoxides to give cyclic or polymeric carbonates.[6] It has been suggested that these reactions involve a zwitterionic adduct between the base and CO_2 for 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), which are the most commonly used amidine and guanidine species in these transformations.[2,6–8] The existence of such base–CO_2 adducts



DBU–CO_2



TBD–CO_2

was also invoked in the reversible fixation of CO_2 by polymers bearing DBU moieties or aromatic nitrogen bases.[9] While these base–CO_2 adducts are expected to be more stable for amidines and guanidines than for amines because they are capable of greater charge delocalization in the former cases, it was proposed from kinetic studies that such a zwitterionic adduct $R_2NH–CO_2$ would be a first intermediate in the synthesis of alkyl ammonium alkyl carbamates $[R_2NH_2][R_2NCO_2]$ from CO_2 and primary or secondary amines.[10] Formation of such adducts would also occur between CO_2 and the free amino groups of proteins.[11] Despite their ubiquity from biology to materials science, all attempts to isolate and characterize a zwitterionic adduct between CO_2 and a nitrogen base, especially an amidine or guanidine molecule such as DBU and TBD, were unsuccessful but led in some cases to the formation of the corresponding bicarbonate salt $[baseH][HCO_3]$ owing to the presence of adventitious water.[7,8] Herein we present the synthesis and characterization, including the X-ray crystal structure, of TBD–CO_2; we also analyze the geometry and electronic structure of this adduct by DFT and MP2 calculations including solid or solvent effects.

First, an off-white powder of the bicarbonate salt $[TBDH][HCO_3]$ was readily obtained upon diffusion of CO_2 into a THF or MeCN solution of TBD in the presence of ambient moisture; colorless crystals were formed after the suspension was heated under reflux. The structure is shown in Figure 1 together with selected bond lengths and angles. The

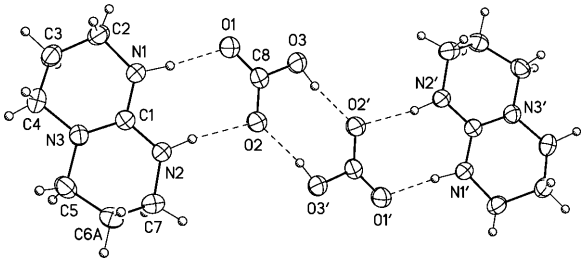


Figure 1. View of the dimer of $[TBDH][HCO_3]$. Displacement ellipsoids are drawn at the 50% probability level. Only one position of the disordered atom C6 is represented. Symmetry code: $'=1-x, 1-y, 2-z$. Selected bond lengths [Å] and angles [°]: C1–N1 1.333(2), C1–N2 1.340(2), C1–N3 1.334(2); N1-C1-N2 118.29(14), N1-C1-N3 121.21(14), N2-C1-N3 120.51(14).

cation and anion are associated through two hydrogen bonds between the nitrogen and oxygen atoms (N1···O1 2.746(2) Å, N2···O2 2.836(2) Å), and two cation–anion pairs form a centrosymmetric dimer, which arises from two hydrogen bonds between the O2 and O3 atoms of two $[HCO_3]^-$ anions (O2···O3′ 2.635(2) Å). This dimeric assembly is identical to that adopted by the amidinium bicarbonate $[PMDBDH][HCO_3]$ (PMDBD = 3,3,6,9,9-pentamethyl-2,10-diazabicyclo-

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[4,4,0]dec-1-ene),[7a] but the structure of [TBDH][HCO_3] is different from those of the other two crystallographically characterized guanidinium bicarbonates, [$C(NH_2)_3$][HCO_3][12a] and [TBNH][HCO_3] (TBN = 1,4,6-triazabicyclo-[3.4.0]non-4-ene),[12b] which exist as infinite hydrogen-bonded chains in which the cations alternate with one or two anions, respectively. These structures can be considered as models for the bicarbonate anion binding site of the transferrins.[12a] The three C1–N bonds of $[TBDH]^+$ are nearly identical in length, with an average value of 1.336(3) Å, reflecting an ideal guanidinium cation as in [TBDH]X with X = NO_2 (1.334(2) Å),[13a] $MeCO_2$ (1.332(3) Å),[13b] BPh_4 (1.336(11) Å), or Cl (1.334(2) Å).[13c] The IR spectrum of [TBDH][HCO_3] in Nujol mull exhibits a strong absorption band centered at 1660 cm^{-1} assigned to asymmetric CN stretching,[13b,14] while the absorption corresponding to the asymmetric CO_3 stretch of the bicarbonate ion is detected at 1600 cm^{-1}.

Diffusion of CO_2 into a THF solution of TBD under strictly anhydrous conditions led to the immediate precipitation of an off-white powder of TBD–CO_2, and colorless crystals were grown after the suspension was heated at 70 °C in a CO_2 atmosphere. A view of the crystal structure of the adduct is shown in Figure 2 together with selected bond lengths and angles. The molecule is almost planar, with only

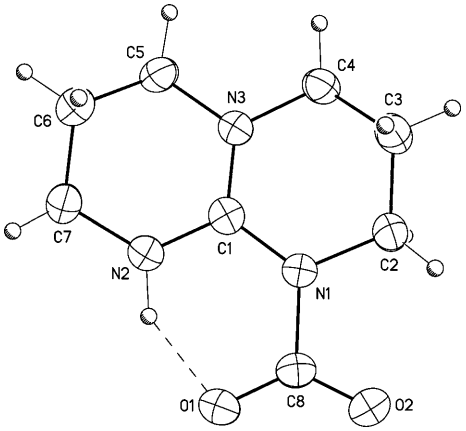

Figure 2. View of TBD–CO_2. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: C1–N1 1.369(3), C1–N2 1.332(2), C1–N3 1.338(3), N1–C8 1.480(3), O1–C8 1.257(3), O2–C8 1.229(2); N1-C1-N2 118.42(19), N1-C1-N3 121.09(17), N2-C1-N3 120.49(19), N1-C8-O1 117.18(18), N1-C8-O2 114.22(17), O1-C8-O2 128.59(19).

C3 and C6 being 0.680(3) and 0.577(3) Å, respectively, out of the mean plane defined by the other atoms (root mean square (rms) deviation 0.072 Å). The zwitterionic structure is clearly demonstrated by the presence of both the guanidinium-type delocalized cationic system, characterized by the planar C1N1N2N3 unit (rms deviation 0.0015 Å) with a mean C1–N distance of 1.346(16) Å, and the carboxylate-type anionic part C8O1O2 with an average C–O distance of 1.243(14) Å. The cationic and anionic fragments are linked by the N1–C8 bond of 1.480(3) Å. This distance is significantly longer than the typical value of 1.35 Å for the N–CO_2 separation in carbamates (1.352(3) Å in methyl benzimidazol-2-yl carbamate (carbendazim)[15a] and 1.382(5) Å in the corresponding benzimidazolium cation[15b,c]). The O1-C8-O2 angle of 128.59(19)° is slightly larger (by ca. 5°) than in carbamates and is in the range of the O-C-O angles measured in η^1 metal CO_2 adducts[16] or N-heterocyclic carbene CO_2 adducts.[17] From these geometrical parameters, the zwitterionic adduct TBD–CO_2 cannot be mistaken for the neutral carbamic acid[18] that would result from CO_2 insertion into the N–H bond of TBD. Also in line with the zwitterionic structure is the position of the H2 atom involved in the hydrogen bond between N2 and O1 (N2···O1 2.535(2) Å), which is much closer to N2 than to O1 (N2–H2 0.95 Å and O1···H2 1.70 Å). It is noteworthy that the zwitterion of carbamic acid H_3NCO_2, which is not stabilized by charge delocalization, was considered as an intermediate between carbamic acid H_2NCO_2H and a mixture of NH_3 and CO_2.[19]

The N1–C8 bond length and O1-C8-O2 angle of TBD–CO_2 are smaller than those of 1.593 Å and 134.6° recently computed by DFT at the B3LYP/6-311++G(d,p) level.[2] To investigate this discrepancy and to analyze the electronic structure of the zwitterionic TBD–CO_2 adduct, wave-function-based as well as DFT calculations were performed both on the isolated compound and also by including the environment as solid or solvent effects (see the Supporting Information for calculation details and results).

Whatever the level of theory, the optimized geometry of isolated TBD–CO_2 (Table S1 in the Supporting Information) differs widely from the experimental one. All the calculations at MP2 and DFT levels (even including dispersion correction in DFT) give similar results on the isolated molecular system. The origin of this drawback cannot be found in the methodology: these results clearly demonstrate that taking account of the environment is essential to obtain a geometry in agreement with the experimental data (Tables S2 and S3 in the Supporting Information). The results from the solid-state DFT/TPSS calculations yield 1.485 Å, 1.640 Å, and 127.8° for the N1–C8, O1···H2, and O1-C8-O2 separations and angle, respectively. Some interactions are indeed only present in the solid state. For example, three intermolecular CH···O hydrogen bonds (with H···O in the range 2.50–2.55 Å) are formed between the CO_2 moiety and three neighboring TBD–CO_2 adducts. With the intramolecular O1···H2 hydrogen bond, each oxygen atom therefore participates in two hydrogen bonds. An induced stacking in the solid state is observed between TBD–CO_2 adducts. The interaction is mainly regulated by the electrostatic and the dispersion interactions (in one unit cell, 42 and 24%, respectively, from the ADF total bonding energy). It is noteworthy that a similar effect is observed when solvent effects are included using a conductor-like screening model with a polar solvent (acetonitrile). In a nonpolar solvent (THF), the optimized geometry approaches that of the isolated system.

The zwitterionic nature is well characterized by the fragment analysis framework provided by the ADF program package.[20] For the X-ray crystal structure of the isolated system, the Hirshfeld DFT/TPSS charges are +0.77 for the TBD fragment and −0.77 for the CO_2 fragment. This result confirms the zwitterionic structure of the adduct, which is also

visualized in Figure 3 with the electrostatic potential mapped onto an isodensity surface. An energy decomposition analysis for TBD–CO_2 was performed on the X-ray crystal structure. The interacting fragments are the guanidinium cation and the

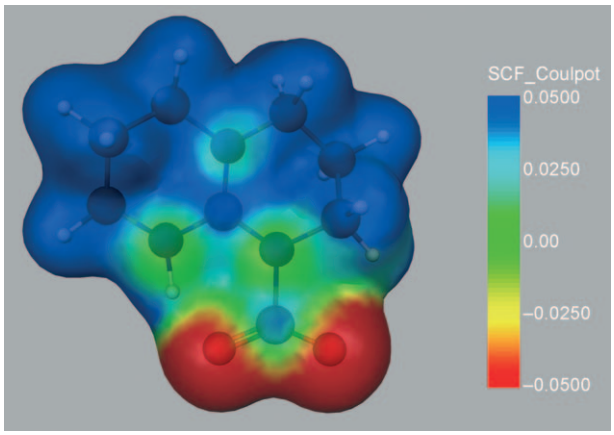

Figure 3. DFT/TPSS molecular electrostatic potential of TBD–CO_2 mapped onto an isodensity surface of 0.01 e Å^{-3}.

carboxylate anion. The results (shown in Table S4 in the Supporting Information) indicate that the stabilization of the adduct (DFT/TPSS bonding energy of $-834\ kJ\,mol^{-1}$) is mainly determined by the orbital component. The electrostatic and the Pauli repulsion components do not compensate each other.

The crystals or powder of TBD–CO_2 were stable at room temperature in a dry atmosphere of argon for at least one month, but loss of CO_2 was observed upon heating at 40 °C under vacuum. Not surprisingly, the TBD–CO_2 adduct was readily transformed into the bicarbonate salt [TBDH][HCO_3] in the presence of water, either in the solid state in air or in solution in wet solvents. The ^{1}H NMR spectra in [D_8]THF revealed that TBD–CO_2 was in equilibrium with TBD; this equilibrium was shifted towards the complete formation of the adduct in the presence of CO_2, while evaporation of the solution afforded the pure guanidine. Only three signals corresponding to the CH_2 units, two triplets and a quintet, in addition to the broad low-field resonance attributed to the NH proton, are detected at 23 °C. This fast limit spectrum shows that TBD–CO_2 undergoes a fluxional process in solution similar to that encountered with TBD ligands in various copper(I) halide complexes and which most likely results from the reversible dissociation of CO_2 and the exchange of the NH proton between the two nitrogen atoms.[21] Upon cooling, the lower-field triplet was resolved into two distinct resonances, consistent with the solid-state structure. The activation energy of $(51.9 \pm 0.7)\ kJ\,mol^{-1}$ for the fluxional process is equal to that measured for [{CuBr(TBD)(PPh_3)}$_2$] ($\Delta G^{\neq} = (51.6 \pm 0.4)\ kJ\,mol^{-1}$).[21b] The zwitterion is more stable towards CO_2 dissociation in the more polar acetonitrile solvent, and no equilibrium with free TBD was observed at 23 °C. The NMR spectra are identical under argon and CO_2 atmosphere. The fluxionality of TBD–CO_2 was, however, observed in acetonitrile, with a higher energy barrier of $(54.1 \pm 0.3)\ kJ\,mol^{-1}$. The IR spectrum of TBD–CO_2 is very different from that of [TBDH][HCO_3], showing the strong ν_{as}(CO) absorption band at 1712 cm^{-1}. The ν_{as}(CN) vibration appears as an intense band centered at 1605 cm^{-1}. These frequencies can be compared with the values obtained from the DFT/PBE solid-state calculations. These values (1661 and 1562 cm^{-1}) must be scaled with respect to the experimental value of 1712 cm^{-1} in order to take anharmonic effects into account; this process gives DFT/PBE values of 1712 and 1610 cm^{-1}, in agreement with the measured data. In contrast, both the calculations on the isolated adduct and those including solvent effects are in disagreement with the measured spectra. The analysis of the vibrational modes reveals a coupling between the C=O and N–C stretching vibrations, despite the dominant contribution given above.

In conclusion, the first isolated nitrogen-base–CO_2 adduct, TBD–CO_2, was synthesized and characterized by working under strictly anhydrous conditions. This compound is stable at room temperature in the solid state or in solution in a polar solvent such as acetonitrile, where it is fluxional, and undergoes CO_2 dissociation under vacuum. The X-ray diffraction analysis and theoretical calculations clearly show the zwitterionic nature of TBD–CO_2, with a N–C(CO_2) distance of 1.48 Å. The synthesis of other adducts between guanidines and CO_2 and the study of their reactivity are in progress; of special interest will be the comparison of the reactions of TBD–CO_2 with those of N-heterocyclic carbene CO_2 adducts and of the recently reported compounds of the type B^+COOA^- in which CO_2 is activated by a frustrated Lewis acid A and Lewis base B pair, as found in tBu$_3$P-(CO_2)B(C_6F_5)$_3$.[22]

Experimental Section

The synthesis and manipulations of TBD–CO_2 were carried out under argon (less than 5 ppm oxygen and water) in anhydrous solvents using Schlenk vessels and vacuum line techniques or in a glove box. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 200 instrument at 23 °C when not otherwise specified; the IR spectra were recorded in Nujol mulls between KBr cell windows on a Bruker Vertex 70 spectrometer.

TBD–CO_2: A flask containing TBD (60.5 mg, 0.43 mmol) in THF (0.5 mL) was frozen in liquid nitrogen, degassed under vacuum, and filled with CO_2 (1 atm). The white powder of TBD–CO_2 was immediately deposited upon warming to 20 °C; the solvent was discarded by decantation, and the product was dried under vacuum (78 mg, 0.42 mmol, 98 %). Elemental analysis (%) calcd for $C_8H_{13}N_3O_2$ (183.20): C 52.45, H 7.15, N 22.93; found: C 51.93, H 7.27, N 22.71. ^{1}H NMR ([D_8]THF, under 1 atm CO_2): $\delta = 12.0$ (br s, 1H, NH), 3.30 (t, $J = 6.0$ Hz, 4H, CH_2), 3.18 (t, $J = 6.0$ Hz, 4H, CH_2), 1.82 ppm (q, $J = 6.1$ Hz, 4H, CH_2). Coalescence of the lower-field triplet was observed at (-10 ± 3) °C. ^{1}H NMR ([D_8]THF, −53 °C, under CO_2): $\delta = 12.8$ (br s, 1H, NH), 3.05 (br s, 2H, CH_2), 3.55 (br s, 2H, CH_2), 3.23 (br m, 4H, CH_2), 1.81 ppm (m, 4H, CH_2). ^{1}H NMR ([D_8]THF, under argon): $\delta = 8.02$ (br s, 1H, NH), 3.17 (t, $J = 6.0$ Hz, 4H, CH_2), 3.03 (t, $J = 6.0$ Hz, 4H, CH_2), 1.76 ppm (q, $J = 6.1$ Hz, 4H, CH_2). ^{1}H NMR ([D_3]MeCN): $\delta = 11.9$ (br s, 1H, NH), 3.49 (t, $J = 6.0$ Hz, 4H, CH_2), 3.28 (t, $J = 6.0$ Hz, 4H, CH_2), 1.92 ppm (m, 4H, CH_2). Coalescence of the lower-field triplet was observed at (-3 ± 1) °C. ^{1}H NMR ([D_3]MeCN, −43 °C): $\delta = 12.10$ (br s, 1H, NH), 3.66 (t, 2H, $J = 6.0$ Hz, CH_2), 3.31 (m, 4H, CH_2), 3.22 (t, $J = 6.0$ Hz, 2H, CH_2), 1.88 ppm (m, 4H, CH_2). ^{13}C{^{1}H} NMR ([D_3]MeCN): $\delta = 154.4$

(CO_2), 154.0 (CN_3), 49.1 (CH_2), 40.9 (CH_2), 21.9 ppm (CH_2). IR: $\tilde{\nu}$ = 1712 (s), 1605 cm^{-1} (vs). Assignment of the signals in the NMR spectra was confirmed with $^{13}CO_2$ experiments. Crystals suitable for X-ray diffraction were obtained by heating a THF solution under CO_2 (1 atm) at 50 °C.

H/D exchange was found to occur at 23 °C between acetonitrile and the NH atoms of TBD and TBD–CO_2; the exchange was complete after 1 h for TBD and after 7 h for the CO_2 adduct.

[TBDH][HCO_3]: According to the same procedure as for TBD–CO_2 but using wet THF as solvent, the white powder of [TBDH][HCO_3] was obtained from TBD (222 mg, 1.59 mmol) in THF (10 mL) after stirring for 30 min at 20 °C. After evaporation to dryness, the product was isolated in quantitative yield (349 mg, 1.59 mmol). Elemental analysis (%) calcd for $C_8H_{15}N_3O_3$ (201.20): C 47.75, H 7.51, N 20.88; found: C 47.36, H 7.64, N 20.56. ^{1}H NMR ([D_3]MeCN): δ = 9.8 (br s, $w_{1/2}$ = 340 Hz, 3H, NH and OH), 3.26 (m, 8H, CH_2), 1.99 ppm (m, 4H, CH_2). $^{13}C\{^1H\}$ NMR ([D_3]MeCN): δ = 164.1 (CO_3), 153.2 (CN_3), 48.0 (CH_2), 39.0 (CH_2), 22.1 ppm (CH_2). IR: $\tilde{\nu}$ = 1660 (vs), 1600 cm^{-1} (s). Crystals suitable for X-ray diffraction were obtained by heating a MeCN solution at 50 °C.

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[1] a) D. B. Dell'Amico, F. Calderazzo, L. Labella, F. Marchetti, G. Pampaloni, *Chem. Rev.* **2003**, *103*, 3857; b) P. G. Jessop, F. Joó, C. C. Tai, *Coord. Chem. Rev.* **2004**, *248*, 2425; c) T. Sakakura, J. C. Choi, H. Yasuda, *Chem. Rev.* **2007**, *107*, 2365.

[2] J. Ma, X. Zhang, N. Zhao, A. S. N. Al-Arifi, T. Aouak, Z. A. Al-Othman, F. Xiao, W. Wei, Y. Sun, *J. Mol. Catal. A* **2010**, *315*, 76.

[3] a) W. McGhee, D. Riley, K. Christ, Y. Pan, B. Parnas, *J. Org. Chem.* **1995**, *60*, 2820; b) W. McGhee, D. Riley, *J. Org. Chem.* **1995**, *60*, 6205.

[4] E. R. Pérez, M. Odnicki da Silva, V. C. Costa, U. P. Rodrigues-Filho, D. W. Franco, *Tetrahedron Lett.* **2002**, *43*, 4091.

[5] J. M. Hooker, A. T. Reibel, S. M. Hill, M. J. Schueller, J. S. Fowler, *Angew. Chem.* **2009**, *121*, 3534; *Angew. Chem. Int. Ed.* **2009**, *48*, 3482.

[6] a) A. Barbarini, R. Maggi, A. Mazzacani, G. Mori, G. Sartori, R. Sartorio, *Tetrahedron Lett.* **2003**, *44*, 2931; b) X. Zhang, N. Zhao, W. Wei, Y. Sun, *Catal. Today* **2006**, *115*, 102; c) X. Zhang, Y. B. Jia, X. B. Lu, B. Li, H. Wang, L. C. Sun, *Tetrahedron Lett.* **2008**, *49*, 6589.

[7] a) E. R. Pérez, R. H. A. Santos, M. T. P. Gambardella, L. G. M. de Macedo, U. P. Rodrigues-Filho, J. C. Launay, D. W. Franco, *J. Org. Chem.* **2004**, *69*, 8005; b) D. J. Heldebrant, P. G. Jessop, C. A. Thomas, C. A. Eckert, C. L. Liotta, *J. Org. Chem.* **2005**, *70*, 5335.

[8] F. S. Pereira, E. R. deAzevedo, E. F. da Silva, T. J. Bonagamba, D. L. da Silva Agostíni, A. Magalhães, A. E. Job, E. R. Pérez González, *Tetrahedron* **2008**, *64*, 10097.

[9] a) B. Ochiai, K. Yokota, A. Fujii, D. Nagai, T. Endo, *Macromolecules* **2008**, *41*, 1229; b) K. D. Vogiatzis, A. Mavrandonakis, W. Klopper, G. E. Froudakis, *ChemPhysChem* **2009**, *10*, 374.

[10] a) P. V. Danckwerts, *Chem. Eng. Sci.* **1979**, *34*, 443; b) J. E. Crooks, J. P. Donnellan, *J. Chem. Soc. Perkin Trans. 2* **1988**, 191.

[11] R. H. Griffey, M. Scavini, R. P. Eaton, *Biophys. J.* **1988**, *54*, 295.

[12] a) D. A. Baldwin, L. Denner, T. J. Egan, A. J. Markwell, *Acta Crystallogr. Sect. C* **1986**, *42*, 1197; b) F. A. Cotton, C. A. Murillo, X. Wang, C. C. Wilkinson, *Inorg. Chem.* **2006**, *45*, 5493.

[13] a) A. Meetsma, E. van Aken, H. Wynberg, *Acta Crystallogr. Sect. C* **1992**, *48*, 1874; b) F. A. Cotton, D. J. Timmons, *Polyhedron* **1998**, *17*, 179; c) U. Wild, P. Roquette, E. Kaifer, J. Mautz, O. Hübner, H. Wadepohl, H. J. Himmel, *Eur. J. Inorg. Chem.* **2008**, 1248.

[14] a) M. Drozd, *Mater. Sci. Eng. B* **2007**, *136*, 20; b) T. Todorova, O. Kröcher, B. Dellev, *J. Mol. Struct. Theochem* **2009**, *907*, 16.

[15] a) V. I. Sokol, V. V. Davidov, M. A. Porai-Koshits, B. E. Zaitsev, M. V. Palishkin, G. V. Sheban, V. I. Pakhomov, S. S. Kukalenko, *Russ. Chem. Bull.* **1988**, *37*, 1148; b) K. Sepassi, T. Sanghvi, S. H. Yalkowsky, *Acta Crystallogr. Sect. E* **2006**, *62*, o4403; c) K. Sepassi, G. S. Nichol, S. H. Yalkowsky, *Acta Crystallogr. Sect. E* **2006**, *62*, o5172.

[16] a) J. C. Calabrese, T. Herskovitz, J. B. Kinney, *J. Am. Chem. Soc.* **1983**, *105*, 5914; b) H. Tanaka, H. Nagao, S. M. Peng, K. Tanaka, *Organometallics* **1992**, *11*, 1450.

[17] a) L. Delaude, *Eur. J. Inorg. Chem.* **2009**, 1681; b) H. Zhou, W. Z. Zhang, C. H. Liu, J. P. Qu, X. B. Lu, *J. Org. Chem.* **2008**, *73*, 8039; c) H. A. Duong, T. N. Tekavec, A. M. Arif, J. Louie, *Chem. Commun.* **2004**, 112.

[18] a) M. Aresta, D. Ballivet-Tkatchenko, D. B. Dell′Amico, M. C. Bonnet, D. Boschi, F. Calderazzo, R. Faure, L. Labella, F. Marchetti, *Chem. Commun.* **2000**, 1099; b) X. M. Yang, *Acta Crystallogr. Sect. E* **2007**, *63*, o4453.

[19] N. Wen, M. H. Brooker, *J. Phys. Chem.* **1995**, *99*, 359.

[20] a) ADF2009.01, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com, **2009**; b) G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. F. Guerra, S. J. A. van Gisbergen, J. G. Snijders, T. Ziegler, *J. Comput. Chem.* **2001**, *22*, 931.

[21] a) S. H. Oakley, M. P. Coles, P. B. Hitchcock, *Inorg. Chem.* **2003**, *42*, 3154; b) S. H. Oakley, D. B. Soria, M. P. Coles, P. B. Hitchcock, *Dalton Trans.* **2004**, 537.

[22] a) C. M. Mömming, E. Otten, G. Kehr, R. Fröhlich, S. Grimme, D. W. Stephan, G. Erker, *Angew. Chem.* **2009**, *121*, 6770; *Angew. Chem. Int. Ed.* **2009**, *48*, 6643; b) G. Ménard, D. W. Stephan, *J. Am. Chem. Soc.* **2010**, *132*, 1796.

