

Geminal Phosphorus/Aluminum-Based Frustrated Lewis Pairs: C–H versus C≡C Activation and CO₂ Fixation**

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Frustrated Lewis pairs (FLPs),^[1] which have donor and acceptor sites in close proximity, are of considerable interest for the dipolar activation of small molecules, such as hydrogen,^[2] alkynes,^[3] and the greenhouse gases carbon dioxide^[4] and nitrous oxide.^[5] So far, phosphines,^[1,6] amines,^[7] thioethers,^[3c] and carbenes^[2e,8] have been applied as Lewis base, while polyfluorinated boranes are the common Lewis acid in FLP chemistry. Surprisingly, alanes have only been rarely used,^[3a,c,9] although these are generally better Lewis acids^[10] that can circumvent the need for decorating the acceptor site with electron-withdrawing fluorinated substituents. Herein we present a simple one-step synthesis of geminal phosphorus/aluminum-based FLPs by hydroalumination^[11,12] of readily available alkynylphosphines,^[13] as well as on their propensity to activate small molecules.^[14]

To illustrate the diversity of our general method, Mes₂PCrBu (**1**; Mes = 2,4,6-Me₃C₆H₂) was treated with di(neopentyl)aluminum hydride, and Mes₂PC≡CC₆H₅ (**2**) was treated with di(*tert*-butyl)aluminum hydride at room temperature, which afforded the respective adducts **3** and **4** as sole products (Scheme 1). Interestingly, phosphinoalanes **3** ($\delta(^{31}\text{P}) = -32.0$ ppm, $^3J(\text{H,P}) = 37.9$ Hz) and **4** ($\delta(^{31}\text{P}) = -14.2$ ppm, $^3J(\text{H,P}) = 17.7$ Hz) both have distinct $^3J(\text{H,P})$

couplings, indicating different conformations of the double bond. The molecular structures of **3** and **4** were established unequivocally by X-ray crystal structure determinations (Figure 1),^[15] which showed that **3** is the expected *cis* hydro-

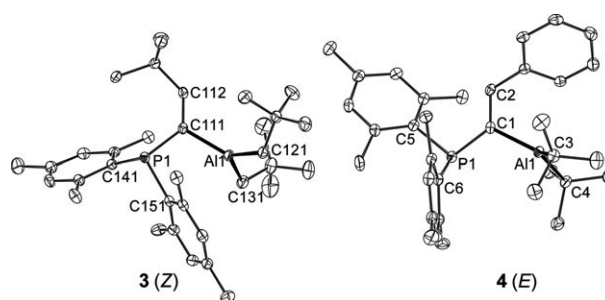
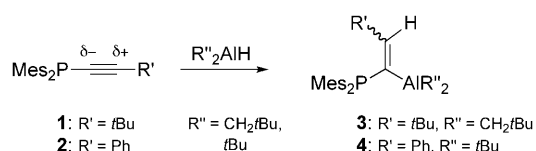


Figure 1. Molecular structures of **3** and **4**. Ellipsoids set at 30% probability; hydrogen atoms are omitted for clarity. Selected average bond lengths [pm] and angles [°] for **3**: Al1–C111 198.0, P1–C111 183.0, C111–C112 133.6, Al1...P1 315.3; Al1–C111–P1 111.0. **4**: Al1–C1 199.2, P1–C1 182.2, C1–C2 134.3, Al1...P1 328.7; Al1–C1–P1 119.1.

alumination adduct with a *Z* configured C=C bond, while a *cis*/*trans* isomerization occurred in the case of *E*-**4**.^[16] Such an isomerization requires intermolecular activation,^[17] which is evidently impeded by the bulky *tert*-butyl group on the double bond in **3**. The highly selective attack of the positively charged aluminum atom at the α -carbon atom of the alkynylphosphines **1** and **2** is in accord with the charge separation in the starting alkyne (NBO values of **1**: $\alpha\text{-C} -0.49$, $\beta\text{-C} +0.03$; **2**: $\alpha\text{-C} -0.35$, $\beta\text{-C} -0.004$). Expectedly, the phosphorus atoms in **3** and **4** have a pyramidal coordination and the aluminum atoms are trigonal-planar. Furthermore, both heteroatoms are perfectly oriented for small-molecule activation.

To investigate the reactivity of our new FLPs, we examined the reaction of **4** with terminal acetylenes, CO₂, and H₂ and we also analyzed the reaction profiles computationally. Treating FLP **4** with phenylacetylene in toluene at room temperature gave a 3:1 mixture of **5a** ($\delta(^{31}\text{P}) = -5.1$ ppm) and **6a** ($\delta(^{31}\text{P}) = 24.2$ ppm, $^3J(\text{H,P}) = 60.1$ Hz; Scheme 2), while at 50 °C a 1:1 mixture was obtained. Heating the mixture at 70 °C for 1 hour resulted in the full conversion of **5a** into **6a**, which after crystallization was isolated in 91 % yield. Single-crystal X-ray diffraction analysis revealed that **6a** is formed by P/Al addition to the alkyne^[3a,b] (Figure 2).^[15] Whereas **5a** could not be obtained in pure form, its large $^1J(\text{H,P})$ coupling of 503.5 Hz is characteristic for a P–H species, indicating that it is formed by C–H activation of the alkyne.^[3a] This hypothesis was confirmed by the reaction of **4**



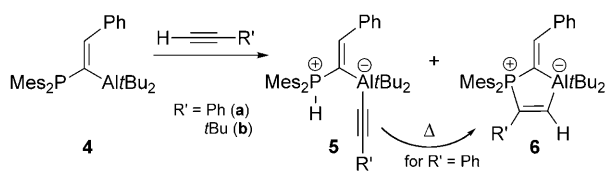
Scheme 1. Synthesis of FLPs **3** and **4** by hydroalumination of **1** and **2**.

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Scheme 2. Reaction of FLP **4** with terminal alkynes.

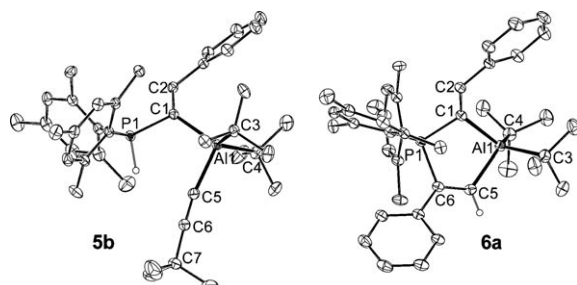


Figure 2. Molecular structures of **5b** and **6a**. Ellipsoids set at 30% probability; hydrogen atoms except at P1 (**5b**) and C5 (**6a**) and toluene (**5b**) or hexane (**6a**) solvent molecules are omitted for clarity. Selected average bond lengths [pm] and angles [°] for **5b**: Al1–C5 198.7(3), P1–H1 127(2), C5–C6 120.3(3), C1–C2 135.0(3); Al1–C5–C6 171.1(2). **6a**: Al1–C5 202.6(3), P1–C6 181.9(3), C1–C2 134.1(4), C5–C6 134.1(4); Al1–C1–P1 106.1(1).

with *tert*-butylacetylene at 40 °C (2 h), which afforded only **5b** (92 %; $\delta(^{31}\text{P}) = -5.2$ ppm, $^1J(\text{H},\text{P}) = 507.5$ Hz) and could be characterized crystallographically (Figure 2). The molecular structure of **5b** reveals a phosphonium alkynylaluminumate with typical Al–C and C≡C bond lengths of $\delta = 198.7$ and 120.3 pm, respectively.

To provide insight into the mode of activation and to establish whether **6a** is a primary product or formed by **5a**, we resorted to M06-2X/6-31 + G(d,p) calculations^[18] on the full system. Three van der Waals complexes were observed upon reacting phenylacetylene with FLP **4** of which the most stable complex (**vdW**, $\Delta E = -5.7$ kcal mol^{−1}; Figure 3) has the alkyne positioned near the aluminum atom^[3a,b,19] and orthogonal to the P–C–Al plane of **4**. Rotating the alkyne into the P–C–Al plane either clockwise or anticlockwise determines the reaction outcome by bringing about the other complexes, namely **5a-vdW** and **6a-vdW** ($\Delta\Delta E = 1.2$ and 2.2 kcal

mol^{−1}, respectively). In **5a-vdW**, the acetylenic proton is oriented towards the Lewis base, which yields **5a** by deprotonation after initial formation of the Al–C bond and subsequent migration of H to P ($\Delta\Delta E^\ddagger = 7.6$, $\Delta\Delta E = -10.7$ kcal mol^{−1}; Figure 3). In **6a-vdW**, the C≡C bond is facing both phosphorus and aluminum atoms, facilitating an asynchronous 1,2-addition by Al–C and then P–C bond formation ($\Delta\Delta E^\ddagger = 4.5$, $\Delta\Delta E = -27.2$ kcal mol^{−1}; Figure 3). It can be concluded that products **5a** and **6a** are formed depending on the initial orientation of the alkyne. Upon heating, **5a** can interconvert via **vdW** into the thermodynamically favored **6a**, which corroborates with the experimental details. Using *tert*-butylacetylene as substrate, **5b** is the thermodynamic sink that does not rearrange into **6b** owing to steric crowding in the transition state (compare with **TS6a** in Figure 3), which precludes the formation of the P–C bond under the reaction conditions.

The behavior of **4** with terminal alkynes encouraged us to examine the FLP activation of CO₂, for which there are only limited examples.^[4,9] CO₂ was bubbled through a solution of **4** in toluene at room temperature for 30 seconds, which after crystallization afforded CO₂ adduct **7** in 74 % yield ($\delta(^{31}\text{P}) = 5.6$ ppm; $\delta(^{13}\text{C})$ (CO₂) = 165.1 ppm, $^1J(\text{C},\text{P}) = 106.5$ Hz). A crystal structure determination confirmed the five-membered heterocycle (Figure 4)^[15] bearing short C–O (128.0 pm) and C=O (120.6 pm) bonds,^[4a] but an elongated P–C(O) bond (191.9 pm). This carbon dioxide binding can be reversed: Treatment of **7** in the solid state at 135 °C under vacuum for 2 minutes resulted in the complete reformation of FLP **4**.

Analysis of the formation of CO₂ adduct **7** at the M06-2X/6-31 + G(d,p) level of theory^[18] showed the intermediacy of a

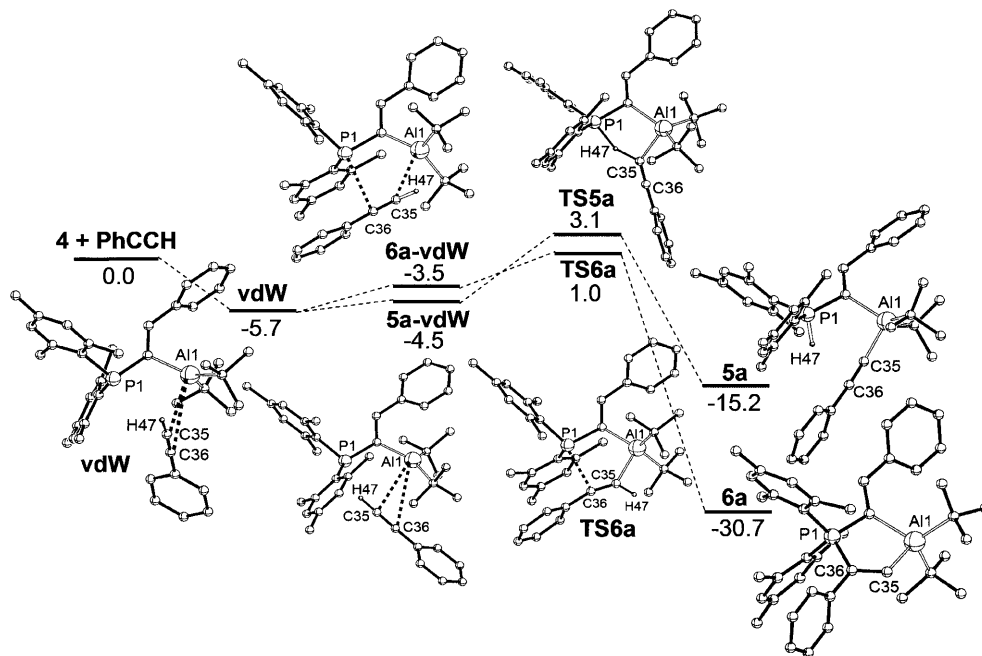


Figure 3. Relative M06-2X/6-31 + G(d,p) energies [kcal mol^{−1}] for the reaction of FLP **4** with phenylacetylene, yielding products **5a** and **6a**. Selected bond lengths [pm] for **vdW**: Al1–C35 299.8, Al1–C36 353.1, C35–C36 121.2. **5a-vdW**: Al1–C35 353.8, Al1–C36 389.3, C35–C36 121.1. **6a-vdW**: Al1–C35 359.3, P1–C36 317.1, C35–C36 121.1. **TS5a**: Al1–C35 214.9, P1–H47 175.0, C35–H47 129.6. **TS6a**: Al1–C35 283.5, P1–C36 217.6, C35–C36 124.8. **5a**: Al1–C35 200.4, P1–H47 139.3, C35–C36 122.6. **6a**: Al1–C35 203.4, P1–C36 183.6, C35–C36 134.8.

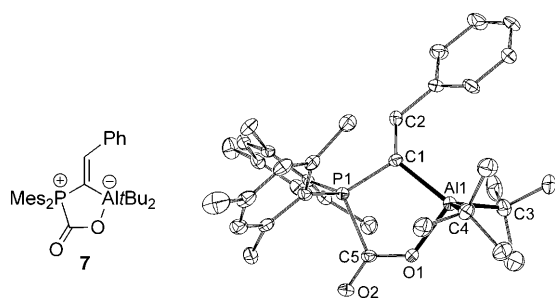


Figure 4. Molecular structure of **7**. Ellipsoids set at 30% probability; hydrogen atoms and toluene molecule are omitted for clarity. Selected average bond lengths [pm] and angles [°] for four independent molecules: Al1–C1 205.8, Al1–O1 185.9, P1–C1 178.8, P1–C5 191.9, C1–C2 134.6, C5–O1 128.0, C5–O2 120.6; Al1–C1–P1 108.6, O1–C5–O2 126.7.

van der Waals complex (**7-vdW**, $\Delta E = -6.52$ kcal mol⁻¹) with a nonlinear CO₂ fragment (171.0°) positioned perpendicular to the P–C–Al plane of **4** (Figure 5). Compound **7-vdW** has a short contact between the oxygen atom of CO₂ and aluminum (222.9 pm), but a rather long P–C distance (298.2 pm) that

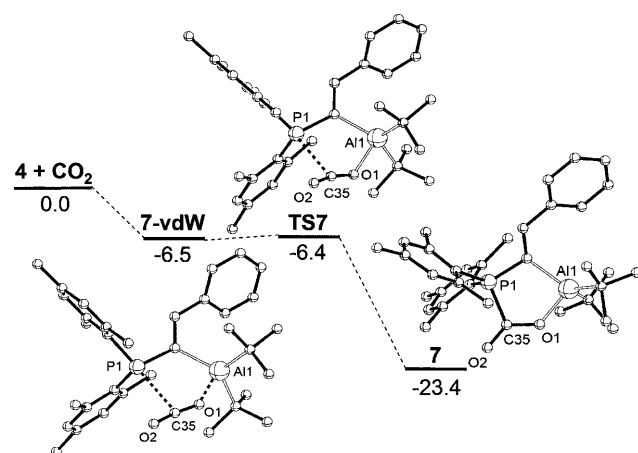


Figure 5. Relative M06-2X/6-31 + G(d,p) energies [kcal mol⁻¹] for the reaction of FLP **4** with CO₂ to give **7**. Selected bond lengths [pm] and angles [°] for **7-vdW**: Al1–O1 222.9, P1–C35 298.2, C35–O1 117.6, C35–O2 115.6; O1–C35–O2 171.0. **7**: Al1–O1 187.9, P1–C35 193.4, C35–O1 127.8, C35–O2 120.8; O1–C35–O2 129.1.

decreases smoothly upon conversion into **7** via an almost barrier-free transition ($\Delta\Delta E^\ddagger = 0.07$, $\Delta\Delta E = -16.9$ kcal mol⁻¹). Interestingly, it has been shown computationally that in the case of P/B-based FLPs, CO₂ interacts first with the Lewis base.^[4a] Our computational analyses show that for the Al-based FLP **4**, both terminal alkynes and CO₂ are activated by initial interaction with the acceptor site, which underscores the fact that alanes are also potent Lewis acids for frustrated Lewis pair chemistry.

Finally, preliminary studies showed that **4** is unreactive towards dihydrogen, but with a very modest endothermicity of $\Delta E = 5.9$ kcal mol⁻¹, calculated at M06-2X/6-31 + G(d,p).^[18] To increase the potential for H₂ activation, the Lewis acidity of the acceptor site and the Lewis basicity of the

donor site can be enhanced easily by using differently substituted P-alkynes and aluminum hydrides.

In summary, hydroalumination of alkynylphosphines provides a facile approach to geminal phosphorus/aluminum-based FLPs, which are ideally suited for small-molecule activation. The full potential of these readily available frustrated Lewis pairs for (catalytic) small molecule activation is currently being explored in our laboratories.

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- [1] D. W. Stephan, G. Erker, *Angew. Chem.* **2010**, *122*, 50–81; *Angew. Chem. Int. Ed.* **2010**, *49*, 46–76.
- [2] a) S. Grimme, H. Kruse, L. Goerigk, G. Erker, *Angew. Chem.* **2010**, *122*, 1444–1447; *Angew. Chem. Int. Ed.* **2010**, *49*, 1402–1405; b) M. Ullrich, A. J. Lough, D. W. Stephan, *Organometallics* **2010**, *29*, 3647–3654; c) T. A. Rokob, A. Hamza, I. Pápai, *J. Am. Chem. Soc.* **2009**, *131*, 10701–10710; d) T. A. Rokob, A. Hamza, A. Stirling, T. Soos, I. Pápai, *Angew. Chem.* **2008**, *120*, 2469–2472; *Angew. Chem. Int. Ed.* **2008**, *47*, 2435–2438; e) D. Holschumacher, T. Bannenberg, C. G. Hrib, P. G. Jones, M. Tamm, *Angew. Chem.* **2008**, *120*, 7538–7542; *Angew. Chem. Int. Ed.* **2008**, *47*, 7428–7432.
- [3] a) M. A. Dureen, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 8396–8397; b) C. Jiang, O. Blacque, H. Berke, *Organometallics* **2010**, *29*, 125–133; c) M. A. Dureen, C. C. Brown, D. W. Stephan, *Organometallics* **2010**, *29*, 6594–6607. For olefins, see: d) J. S. J. McCahill, G. C. Welch, D. W. Stephan, *Angew. Chem.* **2007**, *119*, 5056–5059; *Angew. Chem. Int. Ed.* **2007**, *46*, 4968–4971.
- [4] a) C. M. Mömmling, E. Otten, G. Kehr, R. Fröhlich, S. Grimme, D. W. Stephan, G. Erker, *Angew. Chem.* **2009**, *121*, 6770–6773; *Angew. Chem. Int. Ed.* **2009**, *48*, 6643–6646; b) A. Berkefeld, W. E. Piers, M. Parvez, *J. Am. Chem. Soc.* **2010**, *132*, 10660–10661; c) A. E. Ashley, A. L. Thompson, D. O'Hare, *Angew. Chem.* **2009**, *121*, 10023–10027; *Angew. Chem. Int. Ed.* **2009**, *48*, 9839–9843.
- [5] a) E. Otten, R. C. Neu, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 9918–9919; b) R. C. Neu, E. Otten, D. W. Stephan, *Angew. Chem.* **2009**, *121*, 9889–9892; *Angew. Chem. Int. Ed.* **2009**, *48*, 9709–9712.
- [6] For oligophosphines, see: S. J. Geier, M. A. Dureen, E. Y. Ouyang, D. W. Stephan, *Chem. Eur. J.* **2010**, *16*, 988–993.
- [7] a) V. Sumerin, F. Schulz, M. Nieger, M. Leskelä, T. Repo, B. Rieger, *Angew. Chem.* **2008**, *120*, 6090–6092; *Angew. Chem. Int. Ed.* **2008**, *47*, 6001–6003; b) V. Sumerin, F. Schulz, M. Atsumi, C. Wang, M. Nieger, M. Leskelä, T. Repo, P. Pykkö, B. Rieger, *J. Am. Chem. Soc.* **2008**, *130*, 14117–14119; c) S. J. Geier, A. L. Gille, T. M. Gilbert, D. W. Stephan, *Inorg. Chem.* **2009**, *48*, 10466–10474; d) G. Erös, H. Mehdi, I. Pápai, T. A. Rokob, P. Kiraly, G. Tarkanyi, T. Soos, *Angew. Chem.* **2010**, *122*, 6709–6713; *Angew. Chem. Int. Ed.* **2010**, *49*, 6559–6563. For imines, see: e) P. A. Chase, G. C. Welch, T. Jurca, D. W. Stephan, *Angew. Chem.* **2007**, *119*, 8196–8199; *Angew. Chem. Int. Ed.* **2007**, *46*, 8050–8053. For aromatic *N*-heterocycles, see: f) S. J. Geier, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 3476–3477; g) S. J. Geier, A. L. Gille, T. M. Gilbert, D. W. Stephan, *Inorg. Chem.*

- 2009, 48, 10466–10474; h) S. J. Geier, P. A. Chase, D. W. Stephan, *Chem. Commun.* **2010**, 46, 4884–4886.
- [8] a) P. A. Chase, D. W. Stephan, *Angew. Chem.* **2008**, 120, 7543–7547; *Angew. Chem. Int. Ed.* **2008**, 47, 7433–7437; b) M. Alcarazo, C. Gomez, S. Holle, R. Goddard, *Angew. Chem.* **2010**, 122, 5924–5927; *Angew. Chem. Int. Ed.* **2010**, 49, 5788–5791.
- [9] a) G. Ménard, D. W. Stephan, *J. Am. Chem. Soc.* **2010**, 132, 1796–1797; b) Y. Zhang, G. M. Miyake, E. Y.-X. Chen, *Angew. Chem.* **2010**, 122, 10356–10360; *Angew. Chem. Int. Ed.* **2010**, 49, 10158–10162.
- [10] a) A. Y. Timoshkin, G. Frenking, *Organometallics* **2008**, 27, 371–380; b) J. A. Plumley, J. D. Evanseck, *J. Phys. Chem. A* **2009**, 113, 5985–5992; c) A. L. Gille, T. M. Gilbert, *J. Chem. Theory Comput.* **2008**, 4, 1681–1689.
- [11] a) W. Uhl, *Coord. Chem. Rev.* **2008**, 252, 1540–1563; b) W. Uhl, A. Hepp, H. Westenberg, S. Zemke, E.-U. Würthwein, J. Hellmann, *Organometallics* **2010**, 29, 1406–1412; c) W. Uhl, E. Er, A. Hepp, J. Kösters, M. Layh, M. Rohling, A. Vinogradov, E.-U. Würthwein, N. Ghavtadze, *Eur. J. Inorg. Chem.* **2009**, 3307–3316.
- [12] Hydroboration of an alkynylphosphine resulted in *E*-Ph₂PCH=CHB(Mes)₂, see: Z. Yuan, N. J. Taylor, T. B. Marder, I. D. Williams, S. K. Kurtz, L.-T. Cheng, *J. Chem. Soc. Chem. Commun.* **1990**, 1489–1492.
- [13] H. Westenberg, J. C. Slootweg, A. Hepp, J. Kösters, S. Roters, A. W. Ehlers, K. Lammertsma, W. Uhl, *Organometallics* **2010**, 29, 1323–1330.
- [14] For a computational study on geminal FLPs, see: G. Lu, H. Li, L. Zhao, F. Huang, Z.-X. Wang, *Inorg. Chem.* **2010**, 49, 295–301.
- [15] CCDC 796717 (3), 796718 (4), 797001 (5b), 796719 (6a), and 796720 (7) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. For the experimental details of the X-ray crystal structure determinations, see the Supporting Information.
- [16] *E*-4 is more stable than *Z*-4 by 7.9 kcal mol⁻¹ at M06-2X/6-31 + G(d,p).
- [17] W. Uhl, H. R. Bock, M. Claesener, M. Layh, I. Tiesmeyer, E.-U. Würthwein, *Chem. Eur. J.* **2008**, 14, 11557–11564; W. Uhl, M. Claesener, A. Hepp, B. Jasper, A. Vinogradov, L. van Wüllen, T. K.-J. Köster, *Dalton Trans.* **2009**, 10550–10562.
- [18] a) Y. Zhao, D. G. Truhlar, *Acc. Chem. Res.* **2008**, 41, 157–167; b) Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, 120, 215–241; c) B. G. Janesko, *J. Chem. Theory Comput.* **2010**, 6, 1825–1833. DFT calculations were carried out with Gaussian09 (Revision A.02). Inclusion of solvent effects did not change the energy profile (see the Supporting Information).
- [19] G. S. Hair, A. H. Cowley, R. A. Jones, B. G. McBurnett, A. Voigt, *J. Am. Chem. Soc.* **1999**, 121, 4922–4923.