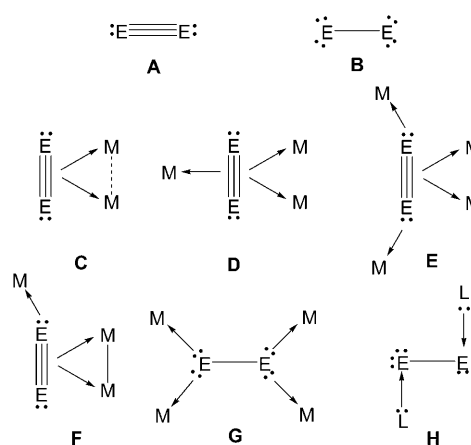


Carbene Stabilization of Diarsenic: From Hypervalency to Allotropy

Mariham Y. Abraham, Yuzhong Wang, Yaoming Xie, Pingrong Wei,
Henry F. Schaefer, III, P. von R. Schleyer,* and Gregory H. Robinson*^[a]

In contrast to nitrogen, the lightest yet most ubiquitous Group 15 element, phosphorus and arsenic exhibit extensive allotropy. Along with the more stable polymeric forms, both white phosphorus and yellow arsenic are well-known tetrahedral allotropes. Indeed, P₄ and As₄ readily pyrolyze to afford P₂^[1] and As₂,^[2,3] respectively, which are well-characterized energetically and spectroscopically in the gas phase,^[4] but are only persistent at high temperatures. Cummins and co-workers demonstrated that it is possible to generate complexes of diphosphorus in condensed phases by mild thermal extrusion of P₂ from niobium diphosphaazide complexes.^[5] We subsequently reported a new class of carbene-stabilized diphosphorus molecules, [L:P–P:L] (L = N-heterocyclic carbenes (NHCs)).^[6] Most recently, Bertrand and co-workers synthesized cyclic(alkyl)(amino)carbene-stabilized P₁ and P₂ complexes by P₄ fragmentation.^[7]

The bond energy of N₂ (226 kcal mol⁻¹) is nearly twice that of P₂ (116 kcal mol⁻¹)^[8] and thrice that of As₂ (83 kcal mol⁻¹),^[9] thus suggesting a diminished importance of p–π bonding among third and fourth period elements.^[10] Consequently, unlike N₂, which usually^[11] exhibits bonding mode **A** (Scheme 1) in its complexes, the E₂ cores in the corresponding diphosphorus and diarsenic complexes may assume either bonding mode **A** (triply bonded dipnictogen) or **B** (singly bonded dipnictinidene; Scheme 1). For example, diarsenic, like diphosphorus, has been known to function as a four-, six-, or eight-electron-donor ligand (**C–G**, Scheme 1) in transition-metal (M)–carbonyl complexes.^[1,2,12,13] An E₂



Scheme 1. Bonding modes for diatomic compounds of Group 15 elements (E = N, P, or As).

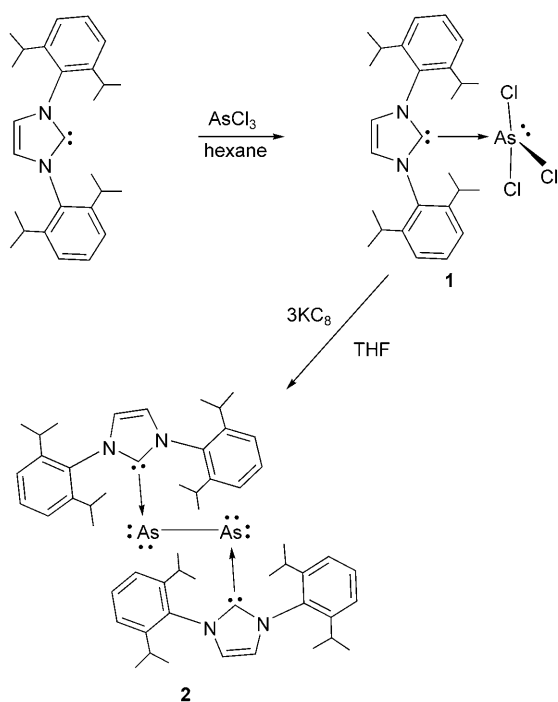
(E = P or As) fragment with an **A**-type structure may be extracted from **C–F**,^[1] whereas the dipnictinidene core (**B**) has been observed in **G**.^[2,13] Is it possible to prepare a carbene-stabilized diarsenic analogue of **H** (Scheme 1)?

We recently demonstrated that NHCs can effectively stabilize highly reactive molecules.^[14–17] Prominent examples of carbene-stabilized complexes not only include diphosphorus,^[6] diborenes ([L:(H)B=B(H):L]),^[18,19] and disilicon ([L:Si=Si:L]),^[20] but this strategy also succeeded in the recent preparation of a neutral metalloaromatic Ga₆ octahedron ([L:Ga(Ga₄Mes₄)Ga:L]).^[21] Herein, we now report the syntheses, X-ray structures, and computations of carbene-stabilized arsenic derivatives of AsCl₃ ([L¹:AsCl₃] (**1**)), and As₂ ([L¹:As–As:L¹] (**2**), L¹ = :C{N(2,6-*i*Pr₂C₆H₃)CH₂}). Compound **2** is the first example of a Lewis base stabilized diarsenic complex.

The hypervalent carbene-stabilized arsenic chloride compound **1** was prepared, in nearly quantitative yield, by the treatment of AsCl₃ with the carbene ligand (L¹:)^[22] (Scheme 2). Subsequent potassium/graphite reduction of **1** affords the carbene-stabilized diarsenic complex, **2**, as air-sensitive red crystals (Scheme 2). The ¹H NMR imidazole

[a] M. Y. Abraham, Dr. Y. Wang, Dr. Y. Xie, Dr. P. Wei,
Prof. H. F. Schaefer, III, Prof. P. von R. Schleyer, Prof. G. H. Robinson
Department of Chemistry and
The Center for Computational Chemistry
The University of Georgia
Athens, GA 30602-2556 (USA)
Fax: (+1) 706-542-9454
E-mail: robinson@chem.uga.edu
schleyer@chem.uga.edu

Supporting information for this article is available on the WWW
under <http://dx.doi.org/10.1002/chem.200902840>.

Scheme 2. Syntheses of carbene-stabilized AsCl_3 (**1**) and diarsenic **2**.

resonances of **1** and **2** are $\delta = 6.47$ and 6.12 ppm, respectively.

The X-ray structure confirms the four coordination of arsenic in **1** as well as the truncated trigonal bipyramidal AsCl_4^- -like “see-saw” geometry (Figure 1). The C(1) and Cl(1) atoms of **1** occupy two equatorial positions; the remaining two Cl atoms are axial (Scheme 3a). These structural features of **1** not only resemble AsCl_4^- , but also the $[\text{L}^2:\text{AsCl}_3]$ adduct ($\text{L}^2 = \text{SC}\{\text{N}(\text{CH}_3)\text{CH}_2\}_2$, **3**).^[23] In contrast, the $\text{:N}(\text{CH}_3)_3$ Lewis base ligand (L^3) in $[\text{L}^3:\text{AsCl}_3]$ (**4**),^[24] occupies one of the two axial positions as shown in Scheme 3b.

This structural distinction may be ascribed to the relatively high electronegativity and small size of the nitrogen center.^[23] Model computations on $[\text{L}^4:\text{AsCl}_3]$ ($\text{L}^4 = \text{:C}\{\text{N}(\text{H})\text{CH}_2\}_2$ **1-H**) not only confirm the preference of the parent L^4 ligand for the equatorial (Scheme 3a) over the axial (Scheme 3b) position, but also reveal the steric effects of the isopropyl groups in **1**. The simplified carbene ligand in **1-H** lines up with the axial chlorines rather than with the equatorial chlorine, as in **1**. The $178.65(13)^\circ$ axial Cl(2)-As(1)-Cl(3) bond angle of **1** equals the 178.7° N-As-Cl angle of **4**, but is larger than the 171.8° Cl(2)-As(1)-Cl(3) angle of **3**, which may be caused by the weak axial chlorine bridging interactions between two neighboring molecules of **3** in the solid state.^[23]

Compound **2**, with C_i symmetry, is isostructural with compound **H** ($\text{E} = \text{P}$; $\text{L} = \text{L}^1$, **5**)^[6] and adopts a *trans*-bent geometry around the As-As bond (the C(1)-As(1)-As(1A)-C(1A) torsion angle = 180° ; Figure 2). The $2.442(1)$ Å central As-As bond length is the same as the bond length of 2.44 Å^[25] in gaseous As_4 and corresponds to the 2.42 Å sum of the ar-

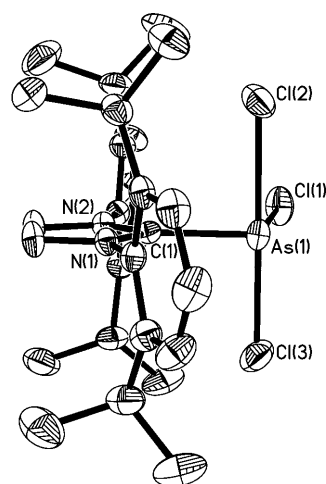


Figure 1. Molecular structure of **1** (thermal ellipsoids represent 30% probability; hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: As(1)-C(1) 2.018(3), As(1)-Cl(1) 2.171(1), As(1)-Cl(2) 2.484(2), As(1)-Cl(3) 2.359(2); C(1)-As(1)-Cl(1) 99.92(10), C(1)-As(1)-Cl(2) 89.09(13), C(1)-As(1)-Cl(3) 90.35(14), Cl(1)-As(1)-Cl(2) 88.23(10), Cl(1)-As(1)-Cl(3) 90.65(8), Cl(2)-As(1)-Cl(3) 178.65(13).

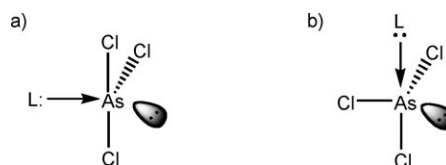
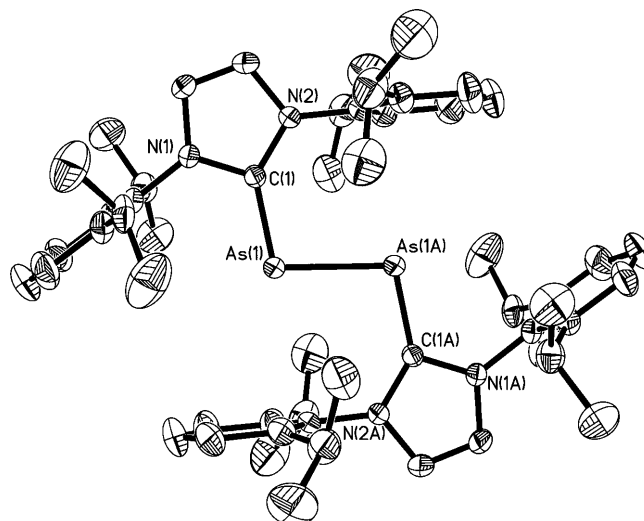
Scheme 3. Structures of $[\text{L}:\text{AsCl}_3]$ complexes.

Figure 2. Molecular structure of **2** (thermal ellipsoids represent 30% probability; hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: As(1)-C(1) 1.881(2), As(1)-As(1A) 2.442(1); C(1)-As(1)-As(1A) 101.11(5), N(1)-C(1)-As(1) 118.98(12), N(2)-C(1)-As(1) 137.63(13).

senic single-bonded covalent radii.^[26] The $101.11(5)^\circ$ C(1)-As(1)-As(1A) bond angle is about 2° less than the $103.19(6)^\circ$ C(1)-P(1)-P(1A) bond angle in **5**, whereas the

As–As bond in **2** is about 0.24 Å longer than the P–P bond of **5** (2.205(1) Å). The 1.881(2) Å As–C_{NHC} bond length in **2** compares well to the reported values for carbene–arsinidene adducts (1.899(3)–1.902(7) Å).^[27] These distances indicate partial As=C double-bond character because they are shorter than the 2.018(3) (Å) value in **1**, but are longer than the typical 1.816–1.827 Å As=C double-bond lengths in acyclic arsaalkenes.^[27] The imidazole rings and the central As–As bond are essentially coplanar in **2**. The 2.0° N(2)–C(1)–As(1)–As(1A) torsion angle is the same as the 2.3° N(2)–C(1)–P(1)–P(1A) torsion angle in **5**, but contrasts with the 90.8° N(2)–C(1)–Si(1)–Si(1A) torsion angle in [L¹:Si=Si:L¹] (L¹: =:C{N(2,6-*i*Pr₂C₆H₃)CH}₂).^[20]

In contrast to *trans*-bent **2**, :As–As: lone pair repulsion in the fully B3LYP/DZP DFT-optimized structure of the simplified [L⁴:As–As:L⁴] (L⁴: =:C(NHCH)₂) model **2-H**^[28] favors a *gauche* conformation with C₂ symmetry and a 93.9° C–As–As–C torsion angle (Figure 3). However, the central As–As

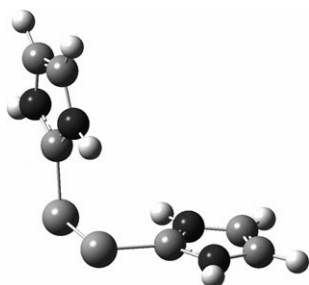


Figure 3. The optimized geometry of the **2-H** model in C₂ symmetry.

single bond rotational barrier in **2-H** is small. The torsion angle discrepancy between **2** and **2-H**, which we also found in the analogous [L:P–P:L] systems,^[6] may be attributed to the substantial steric repulsion between the bulky carbene ligands in **2**. The other computed structural parameters ($d_{\text{As–As}}=2.464$ Å; $d_{\text{As–C}}=1.928$ Å; C–As–As angle = 95.4°) of **2-H** (C₂) agree with the experimental values for **2**.

The localized molecular orbitals (LMOs) of **2-H** were computed in C₁ symmetry by using the X-ray coordinates of **2**.^[28] These LMOs (Figure 4) and natural bond orbital (NBO) analysis support the bonding description (**H**). LMO **a** (Figure 4), depicting the As–As single bond in **2-H** (Wiberg Bond Index (WBI)=1.009), has predominately 4p As character (8.9% s, 90.7% p, 0.4% d). The As–C_{NHC} interaction (WBI=1.341) has partial double-bond character: LMO **b** (Figure 4) depicts the As–C σ bond resulting from :C_{NHC} lone-pair donation to As, whereas LMO **c** (Figure 4) displays the p–π back-donation of the As lone-pair orbital with pure p character (0.0% s, 99.8% p, 0.2% d) to the empty p orbital of C_{NHC}. Although the As–C σ-bond polarization is 67.8% carbon and 32.2% arsenic (As has 15.4% s, 84.3% p, and 0.3% d character), the modest p–π back-donation exhibited in LMO **c** (Figure 4) has 66.3% As and 33.7% C polarization. The remaining As lone-pair orbital (LMO **d**, Figure 4) has predominant s character (76.6% s,

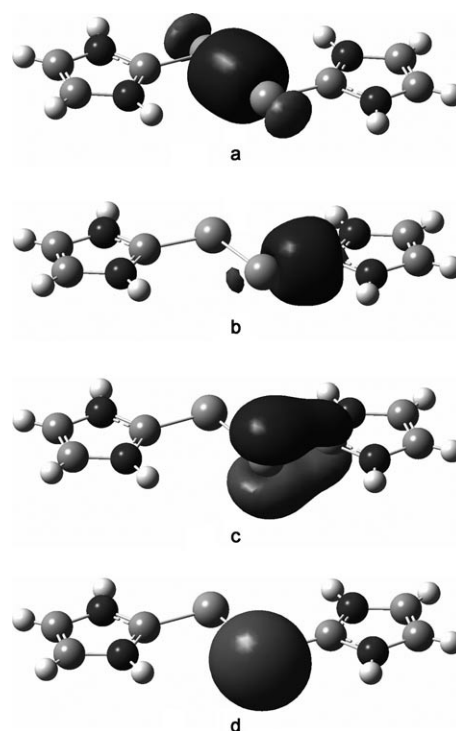


Figure 4. Localized molecular orbitals (LMOs) of **2-H** in C₁ symmetry (based on the X-ray coordinates of **2**). a) As–As σ-bonding orbital; b) As–C σ-bonding orbital; c) lone-pair orbital (mainly p character) with p–π back-donation to the empty p orbital of C_{NHC}; d) lone-pair orbital (mainly s character).

23.3% p, 0.0% d). Compound **2** is not only isostructural to the carbene-stabilized diphosphenidene **5**,^[6] but is also structurally similar to carbene–arsinidene adducts.^[27] Thus, compound **2** can be regarded as a diarsinidene complex.

The utilization of NHCs is a viable means to stabilize highly reactive molecules of nonmetal and metalloid main group elements. Carbene-stabilized diarsenic **2** represents the first Lewis base stabilized diatomic molecule of the Group 13–15 elements, in the formal oxidation state of zero, in the fourth period or higher of the periodic table.

Experimental Section

Synthesis of 1: AsCl₃ (1.63 g, 8.99 mmol) was added to a stirred slurry of the NHC carbene ligand (L¹, 3.50 g, 9.01 mmol) and hexane (50 mL) at ambient temperature. After stirring for a further 21 h, the solvent was removed in vacuo leading to an off-white powder **1** (4.95 g, 96.5%). X-ray quality colorless crystals of **1** were isolated from a solution in toluene/THF at ambient temperature. These gradually decompose and melt at 324°C. ¹H NMR (400 MHz, C₆D₆): δ = 0.93 (d, 12H; CH(CH₃)₂), 1.54 (d, 12H; CH(CH₃)₂), 3.30 (m, 4H; CH(CH₃)₂), 6.47 (s, 2H; NCH), 7.08 (d, 4H; Ar-H), 7.18 (t, 2H; Ar-H). Crystal data for **1**: C₂₇H₃₆AsCl₃N₂, M_r = 569.85, monoclinic, P21/n (No. 14), a = 11.0692(7) Å, b = 13.8303(9) Å, c = 19.2882(12) Å, α = 90.00°, β = 104.3760(10)°, γ = 90.00°, V = 2860.4(3) Å³, Z = 4, R₁ = 0.0465 for 3682 data (I > 2σ(I)), wR₂ = 0.1169 (all data).

Synthesis of 2: THF (60 mL) was added to a flask containing [L¹:AsCl₃] (4.95 g, 8.69 mmol) and KC₈ (3.52 g, 26.07 mmol). After stirring the mix-

ture vigorously for 15 h at ambient temperature, the solvent was removed in vacuo and the residue was extracted with hexane. Concentrating to 4 mL gave X-ray quality single red crystals of **2** overnight at ambient temperature (0.77 g, 19.2%). M.p. 216.5°C; ¹HNMR (400 MHz, C₆D₆): δ = 1.15 (d, 24H; CH(CH₃)₂), 1.49 (d, 24H; CH(CH₃)₂), 3.06 (m, 8H; CH(CH₃)₂), 6.12 (s, 4H; NCH), 7.05 (d, 8H; Ar-H), 7.19 (t, 4H; Ar-H). Crystal data for **2**: C₃₄H₇₂As₂N₄, M_r = 927.0, triclinic, P $\bar{1}$ (No.2), a = 10.842(4) Å, b = 11.160(4) Å, c = 12.592(5) Å, α = 95.640(5)°, β = 112.601(5)°, γ = 108.741(5)°, V = 1288.6(9) Å³, Z = 1, R₁ = 0.0349 for 4685 data (I > 2σ(I)), wR₂ = 0.0890 (all data).

CCDC-748496 (**1**) and CCDC-748495 (**2**) 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.

Acknowledgements

We are grateful to the National Science Foundation for support of this work: CHE-0608142 (G.H.R.), CHE-0716718 (P.v.R.S.), and CHE-0749868 (H.F.S.).

Keywords: allotropy • arsenic • carbenes • density functional calculations • hypervalent compounds

- [1] F. A. Cotton, G. Wilkinson, M. Bochmann, C. Murillo, *Advanced Inorganic Chemistry*, 6th ed., Wiley, New York, **1998**.
- [2] G. Huttner, B. Sigwarth, O. Scheidsteger, L. Zsolnai, O. Orama, *Organometallics* **1985**, *4*, 326–332.
- [3] *Gmelin Handbuch der Anorganischen Chemie, Arsen*, Vol. 17, Verlag Chemie, Weinheim, **1952**.
- [4] K. P. Huber, G. Herzberg, *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*, Van Nostrand, Reinhold, New York, **1979**.
- [5] N. A. Piro, J. S. Figueroa, J. T. McKellar, C. C. Cummins, *Science* **2006**, *313*, 1276–1279.
- [6] Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer III, P. v. R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2008**, *130*, 14970–14971.
- [7] O. Back, G. Kuchenbeiser, B. Donnadiou, G. Bertrand, *Angew. Chem.* **2009**, *121*, 5638–5641; *Angew. Chem. Int. Ed.* **2009**, *48*, 5530–5533.
- [8] W. E. Dasent, *Inorganic Energetics: An Introduction*. 2nd Ed, Cambridge University Press, Cambridge, **1982**.
- [9] Y. Mochizuki, K. Tanaka, *Chem. Phys. Lett.* **1997**, *274*, 264–268.
- [10] W. Kutzelnigg, *Einführung in die Theoretische Chemie, Vol. 2*, Wiley-VCH, Weinheim, **1978**.
- [11] For a range of exceptions, see: D. Roy, A. Navarro-Vazquez, P. v. R. Schleyer, *J. Am. Chem. Soc.* **2009**, *131*, 13045–13053.
- [12] *Advances in Organometallic Chemistry, Vol. 42*, (Eds.: F. G. A. Stone, R. West), Academic Press, San Diego, **1998**.
- [13] O. J. Scherer, M. Eshes, G. Wolmershauser, *Angew. Chem.* **1998**, *110*, 530–533; *Angew. Chem. Int. Ed.* **1998**, *37*, 507–510.
- [14] Y. Wang, G. H. Robinson, *Chem. Commun.* **2009**, 5201–5213.
- [15] R. Wolf, W. Uhl, *Angew. Chem.* **2009**, *121*, 6905–6907; *Angew. Chem. Int. Ed.* **2009**, *48*, 6774–6776.

- [16] D. Scheschkewitz, *Angew. Chem.* **2008**, *120*, 2021–2023; *Angew. Chem. Int. Ed.* **2008**, *47*, 1995–1997.
- [17] C. A. Dyker, G. Bertrand, *Science* **2008**, *321*, 1050–1051.
- [18] Y. Wang, B. Quillian, P. Wei, C. S. Wannere, Y. Xie, R. B. King, H. F. Schaefer III, P. v. R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2007**, *129*, 12412–12413.
- [19] Y. Wang, B. Quillian, P. Wei, Y. Xie, C. S. Wannere, R. B. King, H. F. Schaefer III, P. v. R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2008**, *130*, 3298–3299.
- [20] Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer III, P. v. R. Schleyer, G. H. Robinson, *Science* **2008**, *321*, 1069–1071.
- [21] B. Quillian, P. Wei, C. S. Wannere, P. v. R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2009**, *131*, 3168–3169.
- [22] A. J. Arduengo III, R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marshall, M. Unverzagt, *Tetrahedron* **1999**, *55*, 14523–14534.
- [23] D. J. Williams, C. O. Quicksall, K. J. Wynne, *Inorg. Chem.* **1978**, *17*, 2071–2073.
- [24] M. Webster, S. Keats, *J. Chem. Soc. A* **1971**, 836–838.
- [25] L. R. Maxwell, S. B. Hendricks, V. M. Mosley, *J. Chem. Phys.* **1935**, *3*, 699–709.
- [26] P. Pyykkö, M. Atsumi, *Chem. Eur. J.* **2009**, *15*, 186–197.
- [27] A. J. Arduengo III, J. C. Calabrese, A. H. Cowley, H. V. Rasika Dias, J. R. Goerlich, W. J. Marshall, B. Riegel, *Inorg. Chem.* **1997**, *36*, 2151–2158.
- [28] DFT computations: The **2-H** model was optimized at the B3LYP/DZP level with the Gaussian 94 and Gaussian 03 programs: Gaussian 94, Revision B.3; M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, A. Nanavakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1995**; Gaussian 03, Revision C.02; M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanavakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004** (see the Supporting Information for details). The single-point computation of **2-H** model (C_i symmetry) was performed using the X-ray coordinates of **2**.

Received: October 14, 2009

Published online: November 24, 2009