DALTON
COMMUNICATION

An *ab initio* computational study of monodentate palladium ligand complexes with Möbius-aromatic chiral character †

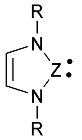
Christian J. Kastrup, Steven V. Oldfield and Henry S. Rzepa *

Department of Chemistry, Imperial College of Science Technology and Medicine, London, UK SW7 2AY

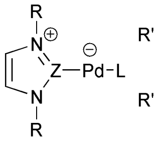
Received 24th April 2002, Accepted 8th May 2002

The 8π homologues 3 of the planar aromatic carbene and silylene ligands 1 are predicted on the basis of *ab initio* B3LYP/DZVP calculations to adopt twisted C_2 geometries resulting from a novel attenuation of ring anti-aromaticity induced by Möbius-type aromaticity, and for which we suggest that appropriately sterically substituted forms might act as chiral mondentate metal ligands in coordination to metals such as palladium.

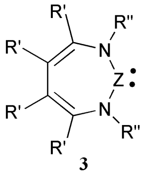
The aromatic heterocyclic carbene/ylid **1** is of much current interest as an alternative to phosphine ligands in metal coordination chemistry, and particularly in palladium complexes and catalysts (*cf.* **2**).[1] We have recently reported[2] that the homologue **3**, although formally an 8π and hence 4*n* electron anti-aromatic heterocycle in the Hückel sense, is predicted on the basis of *ab initio* DFT calculations to distort to a C_2 symmetric chiral form, with an accompanying increase in the Möbius-aromatic character of the ring. Möbius-aromaticity was first predicted in 1964 by Heilbronner,[3] on the basis of Hückel calculations indicating that a cyclic array of p_π containing 4*n* electrons (*n* = 1, 2...) and subjected to an ideally evenly distributed 180° phase shift of the atomic orbitals, would exhibit aromatic resonance stabilisation. With the increasing use of ligands such as **1** in the design of palladium catalysts, we wish to bring attention here to the unusual properties of the homologue (**4**) and to study computationally how the palladium, *via* interaction with the σ framework, might perturb properties such as the chiral inversion barrier and the aromatic/anti-aromatic character of the seven-membered ring.



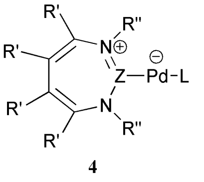
1



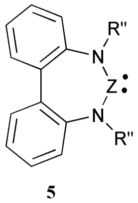
2



3



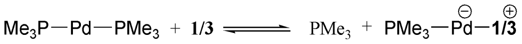
4



5

Calculations † were performed at the B3LYP density functional *ab initio* level,[4] using a double ζ all-electron basis set with polarisation functions (DZVP) for all the elements, which has been shown to result in realistic geometries and energies for complexes of palladium.[5] The aromaticity at the ring centroid was estimated *via* the GIAO–NICS method.[6]

Considering first the computed properties of **1** and **2** (Table 1), we note that the Hückel-aromatic ring in **2** exhibits a typically aromatic NICS value which is perturbed only slightly from the value for the unbound ligand **1**. The ring bond lengths in **2** show little alternation, properties which are essentially unperturbed by coordination to Pd. The displacement of one PMe_3 ligand from the metal by **1** (Scheme 1) is moderately exothermic by 9.4 kcal mol^{-1}.



$$Me_3P{-}Pd{-}PMe_3 + \mathbf{1/3} \rightleftharpoons PMe_3 + PMe_3{-}\overset{\ominus}{Pd}{-}\overset{\oplus}{\mathbf{1/3}}$$

Scheme 1

The homologue **3** in comparison has a NICS value indicative of significant anti-aromaticity, reduced by 4.2 ppm (*i.e.* less anti-aromatic) when the formal carbene is coordinated to the Pd. This is accompanied by a 4° increase in the degree of C_2 twisting of the ligand associated with the greater degree of Möbius character.[3] The energy of PMe_3 displacement (Scheme 1) is largely unperturbed compared to **1**, indicating that **3** should be as effective as **1** in displacing phosphine lignads. Subsequent modelling was with PH_3 replacing PMe_3. This approximation results in over-estimating the phosphine displacement energy by about 4 kcal mol^{-1} (Table 1), since the decreased electron donating capability of PH_3 makes it a less effective ligand.

With R′,R″ = H as the ring substituent, the barrier to inversion of the ring in **4** is very small, as we had previously noted.[2] Our next objective therefore was to investigate if this barrier could be increased to the point where thermal racemisation of an enantiomerically pure ligand could be inhibited. The first system we investigated, R′,R″ = F, is known to have the effect of significantly increasing the Möbius-aromaticity of the ligand.[2] The NICS value of the free ligand (0.3 ppm) makes it in effect non-aromatic, and the degree of twist as measured by the C4–C5–C6–C7 ring dihedral angle increases to 35°. When metal-bound, only a small change in the NICS, to a now slightly negative (aromatic) value is computed. The inversion barrier both for the free and metal-bound ligand is now a more significant 7 kcal mol^{-1}. Commensurate with the increased Mobius aromaticity (reduced Hückel anti-aromaticity) due to the ligand twist, the ring bond lengths show a small reduction in their alternation in both cases.

Introducing steric constraints (R′ = Me) has, as expected, a larger effect on the inversion barrier and the degree of twisting (43°) but less effect than R = F on reducing the anti-aromaticity and, as before, no significant effect on the energy of ligand displacement. A synthetically more realistic ligand (**5**) where the steric constraint is provided by two benzo groups, reveals a high thermal barrier to inversion (and one that could be further increased by appropriate substitution on the benzo group) for the metal bound complex **6**. The final variation we investigated was replacing the carbene centre by a silylene (Z = Si). Examples of such substitution are known for **1** with metals such as Ni and Pt,[7] although surprisingly apparently not for Pd. The 8π electron silyl homologue appears to exhibit a further small increase in the Möbius-aromaticity of the ring, whilst

---

† Electronic supplementary information (ESI) available: Table 1 in html format with links to rotatable 3-D structure diagrams in CHIME format. See http://www.rsc.org/suppdata/dt/b2/b203996f/

DOI: 10.1039/b203996f

Table 1 Computed B3LYP/DZVP energies, geometries and NICS values for **1**–**4**

Structure; substituents	Energy/Hartrees (B3LYP/DZVP)	NICS/ppm	Geometry[a]	ΔE Coordination[b]/ kcal mol^{-1}
1; R = CH_3	−304.8242	−11.8	1.37, 1.39, 1.36; 0.0	—
2; R =CH_3, L = $P(Me)_3$	−5705.7038	−10.8	1.37, 1.39, 1.36, 2.13; 0.0	−9.4
3; Z = C, R,R′,R″ = H	−303.5733	19.2	1.36, 1.43, 1.34, 1.47; 18.45	—
4; Z = C, R,R′,R″ = H, L = $P(Me)_3$	−5704.4513	14.7	1.37, 1.43, 1.34, 1.47, 2.10; 22.43	−8.4
4; Z = C, R,R′,R″ = H, L = PH_3	−5586.4758	15.0	1.36, 1.43, 1.34, 1.47, 2.12; 22.69	−12.5
4; Z = C, R,R′,R″ = H, L = PH_3	−0.5[c]	22.7	1.36, 1.43, 1.34, 1.47, 2.12; 0.0	—
3; Z = C, R = H, R′,R″ = F	−700.5951	0.3	1.37, 1.41, 1.34, 1.45; 34.68	—
4; Z = C, R = H, R′,R″ = F, L = PH_3	−5983.4949	−1.4	1.37, 1.41, 1.34, 1.45, 2.08; 34.06	−10.8
4; Z = C, R = H, R′,R″ = F, L =PH_3	7.1[c]	12.2	1.36, 1.42, 1.34, 1.47, 2.10; 0.0	—
3; Z = C, R,R′,R″ = CH_3	−539.4585	5.6	1.37, 1.45, 1.35, 1.48; 47.59	—
4; Z = C, R,R′,R″ = CH_3, L = PH_3	−5822.3607[d]	3.9	1.37, 1.45, 1.35, 1.48, 2.15; 46.16	−12.3
5; R = CH_3	−689.5161	6.9	1.37, 1.44, 1.41, 1.48; 45.36	—
6; R = CH_3, L = PH_3	−5972.4158	5.3	1.37, 1.44, 1.41, 1.48, 2.14; 43.31	−10.7
6; R = CH_3, L = PH_3	21.7[c]	11.5	1.36, 1.45, 1.43, 1.51, 2.28; 0.0	—
3; Z = Si, R,R′,R″ = H	−555.0256	12.5	1.75, 1.42, 1.35, 1.47; 25.15	—
4; Z = Si, R,R′,R″ = H, L = PH_3	−5837.9274	9.9	1.74, 1.42, 1.35, 1.47, 2.30; 25.70	−12.0
4; Z = Si, R,R′,R″ = H, L = PH_3	0.5[c]	14.8	1.73, 1.42, 1.35, 1.47, 2.30; 0.0	—
3; Z = Si, R = H, R′,R″ = F	−952.0553	−0.8	1.77,1.39,1.34,1.45; 41.40	—
4; Z = Si, R = H, R′,R″ = F, L = PH_3	6234.9566	−2.2	1.75,1.39,1.34,1.45,2.27; 40.79	−11.7
4; Z = Si, R = H, R′,R″ = F, L = PH_3	7.9[c]	8.1	1.74,1.40,1.34,1.40,2.27; 0.0	—

[a] Geometric data: bond length (Å), C2–C3, N3–C4, C4–C5, C5–C6, and Pd–C2 for metal ligand complex; dihedral angle (°), C4–C5–C6–C7. [b] For the equilibrium shown in Scheme 1. [c] Energy of planar form relative to C_2 geometry, in kcal mol^{-1}. [d] Because of the geared methyl interactions, a formal transition state for inversion of chirality proved difficult to locate. We estimate the barrier to be >30 kcal mol^{-1} on the basis of constraining the ring atoms to co-planarity.

again having a very similar ligand displacement energy and ring inversion barrier to the carbon analogue.

We conclude that these carbene and silylene ligands are of an unusual class where their geometry (and hence chirality) is induced by an aromatising trend as a consequence of their partial 8π electron Möbius aromaticity[3] and which we suggest could form the basis for engineering potentially chiral monodentate metal coordination.

Notes and references

1 See for example W. A. Herrmann and C. Kocher, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2162–2187; D. Bourissou, O. Guerret, F. P. Gabbï and G. Bertrand, *Chem. Rev.*, 2000, **100**, 39–91; W. A. Herrmann, V. P. W. Bohm, C. W. K. Gsottmayr, M. Grosehe, C. P. Reisinger and T. Weskamp, *J. Organomet. Chem.*, 2001, **617–618**, 616–628.

2 C. Kastrup, S. V. Oldfield and H. S. Rzepa, *Chem. Commun.*, 2002, 642; W. L. Karney, C. J. Kastrup, S. P. Oldfield and H. S. Rzepa, *J. Chem. Soc., Perkin Trans. 2*, 2002, 388–392; S. Martin-Santamarêa and H. S. Rzepa, *J. Chem. Soc., Perkin Trans. 2*, 2000, 2372–2377; S. Martên-Santamarêa and H. S. Rzepa, *Chem. Commun.*, 2000, 1089.

3 E. Heilbronner, *Tetrahedron Lett.*, 1964, **4**, 1923.

4 Gaussian 98 (Revision A.8), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1998. DZVP basis sets: N. Godbout, D. R. Salahub, J. Andzelm and E. Wimmer, *Can. J. Chem.*, 1992, **70**, 560. Basis set for palladium: N. Godbout, PhD Thesis, Dept. Chim., University of Montreal, Quebec, Canada, 1992. Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, version 11/29/01, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory, Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352, USA. See http://www.emsl.pnl.gov:2080/forms/basisform.html.

5 M. Jakt, L. Johannissen, H. S. Rzepa, D. A. Widowson and R. Wilhelm, *J. Chem. Soc., Perkin Trans. 2*, 2001, 576–581.

6 For references to the NICS technique, see P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao and N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.*, 1996, **118**, 6317; H. Jiao and P. v. R. Schleyer, *J. Phys. Org. Chem.*, 1998, **11**, 655.

7 Ni: T. A. Schmedake, M. Haaf, B. J. Paradise, D. Powell and R. West, *Organometallics*, 2000, **19**, 3263–3265. Pt: B. Gehrhus, P. B. Hitchcock, M. F. Lappert and H. Maciejewski, *Organometallics*, 1998, **17**, 5599–5601.