Pergamon

Tetrahedron Letters, Vol. 35, No. 9, pp. 1365-1366, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $6.00+0.00

0040-4039(94)E0034-U

A Stable Tridentate Carbene Ligand

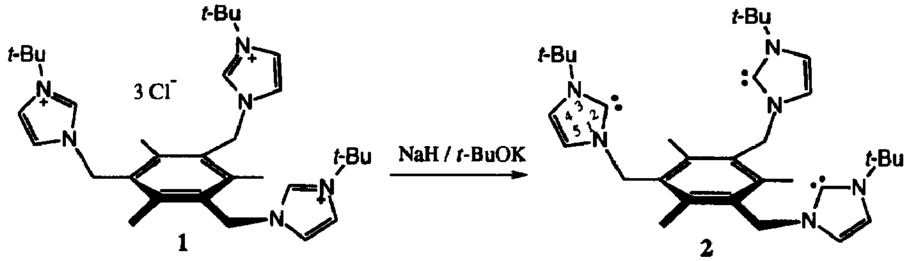
H. V. Rasika Dias* and Wiechang Jin

Department of Chemistry & Biochemistry, The University of Texas at Arlington,
Arlington, Texas 76019-0065, USA.

Abstract: A stable multidentate carbene ligand containing three imidazol-2-ylidenes was synthesized and characterized. The spectroscopic data suggest that there is no intramolecular interaction between the neighboring carbene sites.

The recent synthesis and structural characterization of stable carbenes has attracted considerable attention.[1-3] These nucleophilic carbenes (imidazol-2-ylidenes) are excellent ligands towards a variety of metal ions.[4,5] Here we report the synthesis of a novel compound containing three carbenes (imidazol-2-ylidenes) in proximity. Such compounds would be extremely important in several applications[6] including the synthesis of polycarbene metal complexes.[7]

The compound **2**, [1,3,5-{tris(3-*tert*-butylimidazol-2-ylideno)methyl}-2,4,6-trimethylbenzene] was obtained in good yield by the treatment of its imidazolium salt **1** [1,3,5-{tris(3-*tert*-butylimidazolio)methyl}-2,4,6-trimethylbenzene trichloride] with NaH /*t*-BuOK in THF.[8,9] This tridentate carbene is a stable (under dry N_2) white solid melting at 125-127 °C.



1 **2**

The ^{13}C NMR spectrum (C_6D_6) of **2** shows this to be a very symmetric molecule with signals at δ 215.25 corresponding to C_2 carbons and δ 115.29 and 117.07 due to C_4 and C_5 carbons. These values are typical for imidazol-2-ylidenes.[2] For example the ^{13}C NMR signal for C_2 of the related monodentate compound **3** (1,3-di-*tert*-butlyimidazol-2-ylidene)[10] appears at δ 213.00 and the value for $C_{4,5}$ at δ 114.97. The ^1H NMR spectroscopic data also consistent with the formation of **2**. The resonances for the imidazole ring protons at $C_{4,5}$ positions shift upfield from δ 7.79 and 8.09 for **1** to 6.43 and 6.64 for **2**. Similar trend has been observed for **3** and other monodentate imidazol-2-ylidenes.

One important factor concerning these multidentate carbene compounds is the question of possible intramolecular interaction between the neighboring carbene sites. The spectroscopic and X-ray crystallographic studies involving monodentate imidazol-2-ylidenes show no evidence for any intermolecular interactions even when sterically less demanding substituents are present on the imidazole ring nitrogens.[2] The close similarity of the ^1H and ^{13}C NMR spectroscopic data of **2** to its monodentate analogs suggest that the carbene centers of **2** do not show any significant inter or intramolecular interactions. We are currently investigating the behavior of multidentate carbene ligands containing sterically less demanding substituents (to understand the importance of steric factors) and their metal coordination chemistry.

Acknowledgments: We thank The University of Texas at Arlington for financial support.

REFERENCES AND NOTES:

1. Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361.
2. Arduengo, A. J., III; Dias, H. V. R.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530.
3. Kuhn, N., Kratz, T. *Synthesis* **1993**, 561.
4. Arduengo, A. J., III; Dias, H. V. R.; Calabrese, J. C.; Davidson, F. *Organometallics* **1993**, *12*, 3405.
5. Arduengo, A. J., III; Dias, H. V. R.; Calabrese, J. C.; Davidson, F. *J. Am. Chem. Soc.* **1992**, *114*, 9724.
6. *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; Kluwer Academic Publishers: Norwell, MA, 1988.
7. Herrmann, W. A.; Mihalios, D.; Ofele, K.; Kiprof, P.; Belmedjahed, F. *Chem. Ber.* **1992**, *125*, 1795.
8. All work performed under a dry N_2 atmosphere using Schlenk techniques or a Vacuum Atmospheres HE-493 dry box. The new compounds were characterized by ^1H and ^{13}C NMR spectroscopy. All compounds gave satisfactory C, H and N elemental analysis.
9. The preparation of **1**: The 1,3,5-tris(chloromethyl)-2,4,6-trimethylbenzene (7.0 g, 26 mmol) and 1-*tert*-butylimidazole (10.0 g, 81 mmol) were mixed in 1,4-dioxane (100 mL) and heated at 100 °C for 24 hrs. The resulting solid was collected, rinsed with Et_2O and dried under vacuum to obtain **1** as a white solid (15.3g, 91%), m.p. 240-243 °C. The product can be recrystallized from methylene chloride / diethyl ether mixture. NMR data in DMSO-d_6 : ^1H δ 1.61 (s, $C(C\underline{H}_3)_3$, 27H), 2.28 (s, Ar-$C\underline{H}_3$, 9H), 5.64 (s, $C\underline{H}_2$, 6H), 7.79 (br s, $NC\underline{H}$, 3H), 8.09 (br s, $NC\underline{H}$, 3H), 9.98 (br s, $NC(\underline{H})N$, 3H); $^{13}C\{^1H\}$ δ : 16.24 (Ar-$\underline{C}H_3$), 29.04 ($C\underline{C}H_3$), 47.77 ($\underline{C}H_2$), 59.58 ($\underline{C}Me_3$), 120.17 ($N\underline{C}C$), 122.00 ($N\underline{C}C$), 129.01 (Ar-$\underline{C}$), 134.88 ($N\underline{C}N$), 140.78 (Ar-$\underline{C}$).
   Preparation of **2**: The imidazolium salt **1** (2.0g, 3.13 mmol) and NaH (0.213g, 8.8 mmol) were mixed in THF (25 mL) and stirred for 5 mins to insure good mixing. Then *tert*-BuOK (0.527g, 4.7 mmol) was added to the mixture at room temperature. The color gradually became pale yellow. After 30 min., mixture was filtered through Celite® and washed with toluene. The volatiles were removed from filtrate under vacuum to give a yellow solid. This was recrystallized from diethyl ether and hexanes to obtain **2** as a white solid (0.920g, 56%), m.p. 125-127 °C (dec.). NMR data in C_6D_6: ^1H δ 1.48 (s, $C(C\underline{H}_3)_3$, 27H), 2.37 (s, Ar-$C\underline{H}_3$, 9H), 5.21 (s, $C\underline{H}_2$, 6H), 6.43 (d, J_{HH}=1.4Hz, $NC\underline{H}$, 3H), 6.64 (d, J_{HH}=1.4Hz, $NC\underline{H}$, 3H); $^{13}C\{^1H\}$ δ 16.75 (Ar-$\underline{C}H_3$), 31.39 ($C\underline{C}H_3$), 50.03 ($\underline{C}H_2$), 55.77 ($\underline{C}Me_3$), 115.29 ($N\underline{C}C$), 117.07 ($N\underline{C}C$), 133.55 (Ar-$\underline{C}$), 138.45 (Ar-$\underline{C}$), 215.25 ($N\underline{C}N$).
10. 1,3-di-*tert*-butylimidazol-2-ylidene **3** was synthesized form its imidazolium chloride using a procedure very similar to the published method for the diadamantyl analog (see ref. 2 above), colorless crystals, m.p. : 70-71 °C. NMR data in C_6D_6: ^1H δ 1.52 (s, $C(C\underline{H}_3)_3$, 18H), 6.78 (s, $NC\underline{H}$, 2H); $^{13}C\{^1H\}$ δ 31.47($\underline{C}H_3$), 55.78($\underline{C}Me_3$), 114.97($N\underline{C}C$), 213.00 ($N\underline{C}N$).

(*Received in USA* 22 *November* 1993; *accepted* 22 *December* 1993)