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Nucleophilic Carbenes and the Wanzlick Equilibrium: A Reinvestigation

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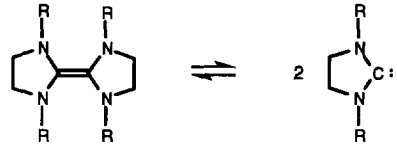
Abstract: Contrary to earlier studies, mixtures of enetetramines A=A and B=B readily exchange their carbene units upon heating (100 – 175 °C) to give the cross-over olefins A=B. The absence of such exchange reactions has formerly been used as evidence against the dissociation of enetetramines into free carbenes by *Lemal et al.* and *Winberg et al.*

Introduction

Electron rich olefins of the enetetramine type $(R_2N)_2C{=}C(NR_2)_2$ were first explored by the groups of *H.-W. Wanzlick* [1] and *N. Wiberg.* [2] These olefins display a pattern of reactivity that is highly unusual for olefins. They are generally air-sensitive [1-4] and can be oxidized to give stable radical cations and even dications. [2, 4] However, their most intriguing property is certainly their facile cleavage to give reaction products that are, at least formally, derived from carbenes $(R_2N)_2C$. Thus, reaction of enetetramines with acids HX results in the formation of aminal derivatives $(R_2N)_2CH\text{-}X$ [1-4]. Carbene complexes $(R_2N)_2C{=}M$ were obtained in good yields from enetetramines and coordinatively unsaturated transition metal complexes. [2] To explain these reactions, a thermal equilibrium between enetetramines **1** and the corresponding "nucleophilic carbenes" **2** has been proposed. [1b, 3] (scheme 1)



1 **2**

	R
1a, 2a	Me
1b, 2b	Et
1c, 2c	*i*-Pr
1d, 2d	Ph
1e, 2e	pTol

Scheme 1

Results and Discussion

After our investigations on isostructural silylenes, [7] germylenes [8] and phosphenium cations [9] and the dimerization of *Wanzlick-carbenes* **2a – 2c**, [6] we were interested to learn under which reaction conditions, if any, the dimerization of carbenes **2** would become reversible. [10] For R = ^{t}Bu, the carbene **2** is stable indefinitely. [6]

Earlier studies seemed to have proven convincingly that Wanzlick's proposed equilibrium does not exist. [11, 12] Dissociation of **1** into carbenes **2** should lead to the formation of non-symmetric olefins A=B (**3**) from

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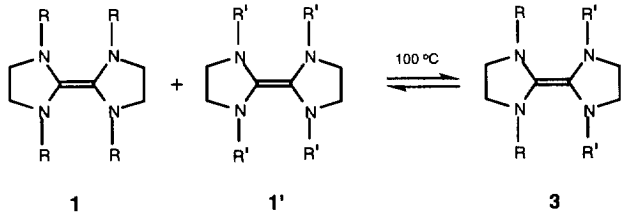
mixtures of **1** and **1'** (Scheme 2). The formation of such mixed olefins had been ruled out in two independent studies. *Lemal et al.* investigated the reaction of **1** (R = Ph) with **1'** (R = *p*-tolyl) and reported the absence of mixed olefins **3d**. [11] *Winberg et al.* studied the thermolysis of **1** (R = Et) + **1'** (R' = n-butyl) and **1** (R = Et) with **1'** = tetrakis(dimethylamino)ethylene without finding evidence for the formation of the mixed olefins. 12

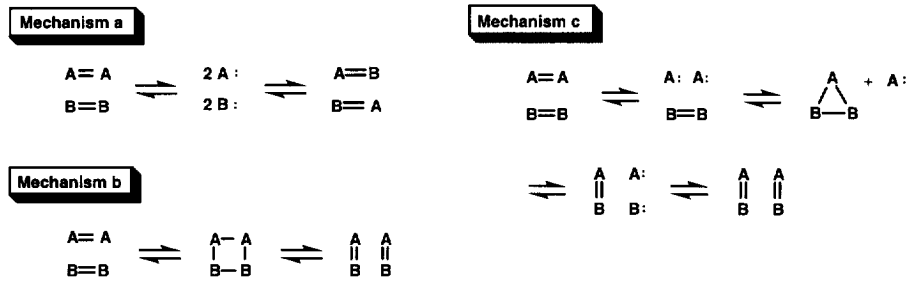
Our preliminary investigation of the pure olefins **1a–1c** by high temperature NMR (150 °C, ^{1}H) did not indicate the presence of free carbenes **2**. [6] However, when we began to investigate mixtures of olefins, we observed the rapid formation of the metathesis products **3a–3d** that had previously been ruled out by *Lemal* and *Winberg*. The mixtures obtained were statistical, i. e. A=A : A=B : B=B = 1 : 2 : 1 in all cases, except for the "Lemal Mixture" **1d** + **1e**. [13,15]



	R	R'
3a	Me	Et
3b	Et	*i*-Pr
3c	*i*-Pr	Me
3d	Ph	pTol

Scheme 2. Catalyst free metathesis of symmetric enetetramines

Our findings support the existence of the Wanzlick equilibrium (**a**), but do not unequivocally prove it because the [2+2]-cycloaddition / [2+2]-cycloreversion of the enetetramines (**b**) would also explain the formation of mixed olefins **3**. [14] A third mechanism, (**c**) requires that the Wanzlick equilibrium exists for *at least one* of the two olefins. [14]



Scheme 3. Catalyst free metathesis of symmetric enetetramines: possible mechanisms

It has been suggested by one of the referees that the metathesis reactions described in this communication are proton catalyzed. Two observations speak against this assumption. 1.) The metathesis reaction is observed even in the presence of molten potassium. 2.) The addition of traces of alcohols or other protic compounds leads to complex product mixtures instead of the metathesis products **3**.

In view of the stability of other carbenes of type $(Do)_2C$, the catalyst free olefin metathesis reaction reported in this study may well be general for olefins of the type Do_4C_2 (Do = Donor).

Experimental Section **1a–1c**, [6] **1e** [1b] and **1d** [1b] were obtained by published procedures and purified by triple sublimation (**1a–1c**), repeated washing with THF (**1e**) or extractive recrystallization (**1d,** Soxhlet extractor, 3 g / 100 mL hexanes, impurities remain undissolved). All olefins were handled under argon (99.995 %) with usual Schlenk techniques or in an inert gas glove box (N_2, M. Braun, H_2O and O_2 < 1 ppm). Equimolar amounts (*ca.* 50 mg) of the olefins were dissolved in the deuterated solvent and the frozen solutions flame-sealed under vacuum in vacuum baked (160 °C / 10^{-4} Torr / 24h) 5 mm NMR tubes. Equilibration was monitored in 15 min intervals by ^{1}H-NMR. Complete equilibration (statistical 1:2:1 mixtures) after 1 / 175 °C (**3b** + **3c**) and 1–2h / 100 °C for all other cases. Aryl substituted derivatives were measured in THF-d^8 to avoid overlap of the ^{13}C signals with the C_6D_6 peaks. NMR solvents (1 % TMS as internal standard) were dried and stored over liquid Na/K alloy in a Young® valve flask under Argon. ^{15}N NMR chemical shifts *vs.* $MeNO_2$ (external) in DMSO. Spectra were measured on a Varian Unity-500 Spectrometer. NMR data of **1a–1c** (^{1}H, ^{13}C and ^{15}N) have been published previously. [6]

1,3-Diethyl-1',3'-dimethyl-2,2'-biimidazolidinylidene (3a, C_6D_6): ^{1}H δ 1.06 (t, 6H, ^3J = 7.1 Hz, $NCH_2C\underline{H}_3$), 2.67 (s, 6H, $NC\underline{H}_3$), 2.77 (s, 4H, $NC\underline{H}_2C\underline{H}_2N$), 2.79 (s, 4H, $NC\underline{H}_2C\underline{H}_2N$), 2.97 (q, 4H, ^3J = 7.1 Hz, $NC\underline{H}_2CH_3$). — ^{13}C δ 12.80 (q, ^1J(C,H) = 124.0 Hz, $NCH_2\underline{C}H_3$), 39.76 (q, ^1J(C,H) = 133.3 Hz, $N\underline{C}H_3$), 46.20 (t, ^1J(C,H) = 134.8 Hz, $N\underline{C}H_2\underline{C}H_2N$), 49.06 (t, ^1J(C,H) = 138.6 Hz, $N\underline{C}H_2\underline{C}H_2N$), 53.17 (t, ^1J(C,H) = 138.48 Hz, $N\underline{C}H_2CH_3$), 125.27 (s, EtN$\underline{C}$=), 129.53 (s, MeN$\underline{C}$=) ;— ^{15}N-NMR δ –321.51 (Et$\underline{N}$), –332.20 (Me$\underline{N}$).

1,3-Diisopropyl-1',3'-dimethyl-2,2'-biimidazolidinylidene (3b, C_6D_6): ^{1}H δ 1.03 (d, 12H, ^3J(H,H) = 6.6 Hz, $CH(C\underline{H}_3)_2$), 2.68 (s, 6H, $NC\underline{H}_3$), 2.71 (s, 4H, $NC\underline{H}_2$), 2.83 (s, 4H, $NC\underline{H}_2$), 3.73 (sep, 2H, ^3J(H,H) = 6.6 Hz, $C\underline{H}(CH_3)_2$). — ^{13}C δ 19.98 (br, q, ^1J(C,H) = 123.4 Hz, $N\underline{C}H(CH_3)_2$), 39.21 (q, ^1J(C,H) = 133.9 Hz, $N\underline{C}H_3$), 43.26 (t, ^1J(C,H) = 140.1 Hz, $N\underline{C}H_2\underline{C}H_2N$), 47.63 (d, ^1J(C,H) = 139.4 Hz, $CH(\underline{C}H_3)_2$), 53.84 (t, ^1J(C,H) = 143.5 Hz, $N\underline{C}H_2$), 122.77 (s, ^{i}PrN$\underline{C}$=C), 128.77 (s, MeN$\underline{C}$); — ^{15}N δ –315.51 (^{i}Pr$\underline{N}$), –330.96 (Me$\underline{N}$).

1,3-Diethyl-1',3'-diisopropyl-2,2'-biimidazolidinylidene (3c, C_6D_6): ^{1}H δ 1.01 (d, 12H, ^3J(H,H) = 6.6 Hz, $CH(C\underline{H}_3)_2$, 1.08 (t, 6H, ^3J(H,H) = 6.9 Hz, $CH_2C\underline{H}_3$), 2.71 (s, 4H, $NC\underline{H}_2$), 2.83 (s, 4H, $NC\underline{H}_2$), 3.09 (q, 4H, ^3J(H,H) = 6.9 Hz, $NC\underline{H}_2CH_3$), 3.94 (sep, 2H, ^3J(H,H) = 6.6 Hz, $C\underline{H}(CH_3)_2$); — ^{13}C δ 13.33 (q, ^1J(C,H) = 124.1 Hz, $NCH_2\underline{C}H_3$), 19.20 (br, q, ^1J(C,H) = 122.7 Hz, $NCH(\underline{C}H_3)_2$), 43.17 (t, ^1J(C,H) = 138.2 Hz, $N\underline{C}H_2\underline{C}H_2N$), 45.20 (t, ^1J(C,H) = 121.8 Hz, $N\underline{C}H_2$), 47.00 (d, ^1J(C,H) = 138.9 Hz, $N\underline{C}H(CH_3)_2$), 49.75 (t, ^1J(C,H) = 138.6 Hz, $N\underline{C}H_2CH_3$), 123.59 (s, $N_2\underline{C}$=), 125.74 (s, $N_2\underline{C}$=); — ^{15}N δ –314.53 (^{i}Pr$\underline{N}$), –318.95 (Et$\underline{N}$).

1,1',3,3'-Tetra-phenyl-2,2'-biimidazolidinylidene (1d, THF-d^8): ^{1}H δ 3.58 (s, 4H, $NC\underline{H}_2$), 6.52, 6.62, 6.91 (m, Ph); — ^{13}C δ 49.37 (t, ^1J(C,H) = 143.5 Hz, $\underline{C}H_2$), 117.71 (d, ^1J(C,H) = 156.7 Hz, *ortho*-$\underline{C}$H), 119.02 (d, ^1J(C,H) = 158.9 Hz, *para*-$\underline{C}$H), 119.58 ($N_2\underline{C}$), 127.80 (dd, ^1J(C,H) = 156.7 Hz, ^2J(C,H) = 8.1 Hz, *meta*-$\underline{C}$H), 145.16 (s, *ipso*-$\underline{C}$H).

1,1',3,3'-tetra-p-tolyl-2,2'-biimidazolidinylidene (1e, THF-d^8): ^{1}H δ 2.11 (s, 12H, $C\underline{H}_3$), 3.75 (s, 8H, $C\underline{H}_2$), 6.56 (d, 8H, ^3J(H,H) = 8.0 Hz), 6.74 (d, 8H, ^3J(H,H) = 8.0 Hz); – ^{13}C δ 20.33 (q, ^1J(C,H) = 125.1 Hz, $\underline{C}H_3$), 49.90 (t, ^1J(C,H) = 143.3 Hz, N-$\underline{C}H_2$), 117.73 (dd ^1J(C,H) = 156.7 Hz, ^2J(C,H) = 4.3 Hz, *ortho*-$\underline{C}$H), 120.71 (s, $N_2\underline{C}$=C), 127.78 (*para*-$\underline{C}$H), 128.32 (d, ^1J(C,H) = 153.0 Hz, *meta*-$\underline{C}$H), 143.49 (*ipso*-$\underline{C}$H).

1,3-Diphenyl-1',3'-di-*para*-tolyl-2,2'-biimidazolidinylidene (3d, THF-d^8): ^{1}H δ 2.11 (s, 3H, $NC_6H_4C\underline{H}_3$), 3.78 (s, 4H, $NC\underline{H}_2$), 3.79 (s, 4H, $NC\underline{H}_2$), 6.65–6.90 (m, 18H, Ph, pTol); – ^{13}C δ 20.32 (q, ^1J(C,H) = 125.1 Hz, $\underline{C}H_3$), 49.14 (t, ^1J(C,H) = 143.7 Hz, Ph–N$\underline{C}H_2$), 50.00 (t, ^1J(C,H) = 143.5 Hz, Tol-N$\underline{C}H_2$), 117.18 (dt, ^1J(C,H) = 156.3 Hz, ^2J(C,H) = 6.9 Hz, *ortho*–Ph), 118.15 (dd, ^1J(C,H) = 156.3 Hz, ^2J(C,H) = 4.7 Hz, *ortho*–Tol), 118.60 (dt, ^1J(C,H) = 158.9 Hz, ^2J(C,H) = 7.3 Hz, *para*–Ph), 119.47 (s, PhN$\underline{C}$=), 121.67 (p-TolN$\underline{C}$=), 127.73 (dd, ^1J(C,H) = 156.3 Hz, ^2J(C,H) = 8.1 Hz, *meta*–Ph), 128.15 (*para*–Tol), 128.29 (*meta*–Tol), 143.07 (*ipso*–Tol), 145.32 (*ipso*–Ph).

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13. This is likely due to the low solubility of **1d** in benzene(**1d** < **3d** < **1e** < **1a–c**).
14. The thermal dimerization of two electron rich olefins is highly unlikely in our opinion, and a similar argument based on the relative electron demand applies to the reaction of an enetetramine with a nucleophilic carbene.
15. Results presented at the *1998 Canadian Society for Chemistry Conference*, May 31 – June 4. 1998, Whistler, BC.