Unprecedented Metathesis of Metal–Carbon and Carbon–Carbon Bonds in α-Agostic *n*-Alkyl Niobium Alkyne Complexes

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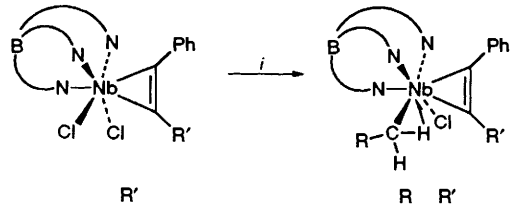
The α-agostic *n*-ethyl and *n*-propyl niobium alkyne complexes [NbL(Cl)(μ-H–CHR)(PhC≡CR′)] [L = hydridotris-(3,5-dimethylpyrazolyl)borate; R = Me, Et; R′ = Me, Et, Pr^n] undergo a thermolytic exchange of the niobium and alkyne-bound alkyl groups to give [NbL(Cl)(R′)(PhC≡CCH$_2$R]; first-order kinetic parameters have been obtained when R = R′ = Me ($\Delta H^{\ddagger}$ = 113 kJ mol^{-1}, $\Delta S^{\ddagger}$ = 4 J K^{-1} mol^{-1}).

Recent studies show that the insertion of an olefin into transition metal–hydrogen or –alkyl bonds, steps of utmost importance in several catalytic processes,[1] are assisted either by β-[2] or α-agostic[3] interactions depending on the complexes involved. We recently described[4] a rare case of isolable α-agostic *n*-ethyl complexes of niobium stabilised by four-electron donor alkyne and hydridotris(3,5-dimethylpyrazolyl)borate (L) ligands, [NbL(Cl)(μ-H–CHMe)(PhC≡CR′)]. Although the latter bonding mode represents a ground-state structure, the *cis* dispostion of both an α-agostic activated ethyl group and a coordinated alkyne might foster the mutual interaction of these ligands. Mechanistically, this could be relevant to some of the reactions cited above. We report in this communication new examples of α-agostic ethyl and *n*-propyl niobium alkyne complexes and their unprecedented thermal rearrangement that exchanges the niobium bound α-agostic group and the alkyne alkyl group.

The α-agostic ethyl and *n*-propyl complexes [NbL(Cl)-(μ-H–CHR)(PhC≡CR′)] (R = Me, R′ = Me **2a**, Et **2b**, Pr^n **2c**, Ph **2d**; R = Et, R′ = Me **3a**, Et **3b**) were synthesized in yields exceeding 80% *via* treatment of the dichloro derivatives [NbLCl$_2$(PhC≡CR′)] **1a–d** with the appropriate chloro Grignard reagent in toluene, according to the procedure[4] we developed for **2a** and **2b** (Scheme 1). Evidence for an α-agostic interaction in the new† ethyl complexes **2c** and **2d** directly follows from that obtained[4] for **2a** and **2b** and is not further discussed here. For the new α-agostic *n*-propyl complexes, similar key spectral data are obtained.† The ^{1}H NMR spectra for the niobium bound *n*-propyl groups are of the more complex ABCDX$_3$ type. The diastereotopic protons of the niobium bound methylene group exhibit a large chemical shift difference ($\Delta\delta$ = 3.1 ppm), one of them being deshielded (δ 3.69 for **3a**) and the other one shielded (δ 0.60 for **3a**). In the ^{13}C NMR spectrum of **3a**, the niobium bound methylene carbon resonates (δ 95.9) as a doublet of doublets with $^1J_{CH}$ = 106 and 125 Hz, giving definitive evidence for the α-agostic interaction.[1a,5]

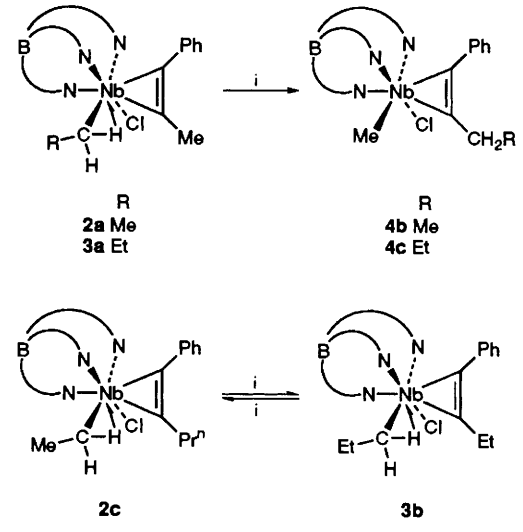
Upon warming to 363 K in toluene, the phenylpropyne *n*-ethyl complex [NbL(Cl)(μ-H–CHMe)(PhC≡CMe)] **2a** undergoes a clean rearrangement leading unexpectedly to the *phenylbutyne methyl* complex† [NbL(Cl)(Me)(PhC≡CEt)] **4b** in *ca.* 80% yield as ascertained by ^{1}H and ^{13}C NMR spectroscopies (Scheme 2). The conversion is virtually complete after *ca.* 36 h on a half-millimole scale. Small amounts of the dichloro complex **1b** (but not **1a**) are also formed. In a similar fashion (Scheme 2), thermolysis of the phenylpropyne α-agostic *n*-propyl complex **3a** affords the *phenylpentyne* derivative [NbL(Cl)(Me)(PhC≡CPr^n)] **4c**, small amounts of the dichloro complex [NbLCl$_2$(PhC≡CPr^n)] **1c** also being formed. The ^{1}H and ^{13}C NMR data obtained after thermolysis are identical with those of authentic samples prepared from **1c** and MeMgCl in toluene.† These chloro methyl derivatives are new compounds. Hence, the unexpected result of these thermolyses is the exchange of the niobium bound α-agostic group and of the methyl group of the coordinated alkyne. The diphenylacetylene α-agostic ethyl complex **2d** is reluctant to undergo this rearrangement. When heated under similar conditions, the σ-benzyl complex[4] [NbL(Cl)(CH$_2$Ph)(PhC≡CMe)] merely decomposes to give numerous ill defined compounds as ascertained by ^{1}H NMR spectroscopy.

The course of these reactions has been studied by ^{1}H NMR in deuteriated toluene. The rearrangement of **2a** and **3a** follows a clean first-order kinetic rate law, no intermediate being observed. In the case of **2a**, an Eyring plot of four different rate constants yields the following activation parameters: $\Delta H^{\ddagger}$ = 113 ± 5 kJ mol^{-1}, $\Delta S^{\ddagger}$ = 4 ± 12 J K^{-1} mol^{-1}. There is no dependence upon the migrating *n*-alkyl

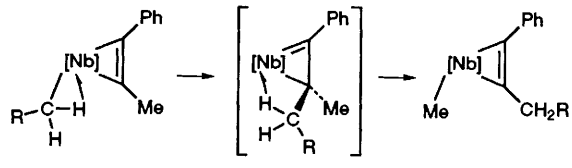


R′	R	R′
1a Me	**2a** Me	Me
1b Et	**2b** Me	Et
1c Pr^n	**2c** Me	Pr^n
1d Ph	**2d** Me	Ph
	3a Et	Me
	3b Et	Et

Scheme 1 *Reagents and conditions*: i, RCH$_2$MgCl, toluene–Et$_2$O, 243 K to room temperature



Scheme 2 *Reagents and conditions*: i, toluene, 338 K or above



Scheme 3 [Nb] = NbLCl

group since at 343 K, the rate constants k for the rearrangement of **2a** and **3a** are equal within experimental error [k_{343} (**2a**) = 3.0 10^{-5} s^{-1}, k_{343} (**3a**) = 2.9 10^{-5} s^{-1}].

Upon heating to 343 K in toluene, both [NbL(Cl)(μ-H–CHMe)(PhC≡CPr^n)] **2c** and [NbL(Cl)(μ-H–CHEt)(PhC≡CEt)] **3b** yield an equilibrating mixture of **2c** and **3b** (Scheme 2). This observation emphasizes the fact that there is a true exchange between the niobium- and alkyne-bound alkyl groups as a whole. We can even define this unprecedented reaction as a real metathesis of a metal–carbon bond and a carbon sp-carbon sp^3 bond of a coordinated alkyne.

At this stage, some comments regarding possible mechanisms seem appropriate. The near zero $\Delta S^{\ddagger}$ value observed for the rearrangement of **2a** points to a transition state closely resembling the starting α-agostic complex. The equilibrium between **2c** and **3b** contrasts with the thermolysis of **2a** which goes to completion. This could reflect the absence of significant α-agostic interaction in the niobium methyl species which disfavours the back reaction. In this respect, the fact that the non-agostic σ-benzyl complex does not undergo the rearrangement is noteworthy. The α-agostic interaction that is needed could assist the direct internal attack of the alkyl on to the alkyne bound carbon forming a transient η^2-alkenyl complex as described in Scheme 3. As a conclusion, it is worth emphasizing the novelty and possible implications of this thermally induced exchange of alkyl groups within the coordination sphere of a transition metal.

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Footnote

† All new compounds gave spectroscopic and/or analytical data in accord with their assigned structures. All the compounds described herein (except **2d**) exist as a mixture of two isomers depending on the orientation of the alkyne with respect to L. *Selected data*: [NbL(Cl)(Et)(PhC≡CPr^n)] **2c** ^{1}H NMR (C_6D_6, 200 MHz): major isomer δ 7.05–6.86 (m, 5H, Ph), 5.73, 5.55, 5.41 (1H each, C*H* of L), 4.07 (m, 2H, ≡CCH_2CH$_2$CH$_3$), 3.84 (m, 1H, NbHC*H*CH$_3$), 2.77, 2.21, 2.10, 2.08, 1.88, 1.59 (3H each, CH_3 of L), 1.24 (t, J = 7.3 Hz, 3H, ≡CCH$_2$CH$_2$CH_3), 1.16 (dd, J = 7.6, 6.2 Hz, 3H, NbCH$_2$CH_3), 0.38 (dq, J = 12.6, 6.1 Hz, 1H, Nb*H*CHCH$_3$); minor isomer (some resonances obscured) δ 8.23 (d, J = 7 Hz, 2H, *o-H* of Ph), 7.45 (t, J = 7.5 Hz, 2H, *m-H* of Ph), 5.69, 5.60 (1H each, C*H* of L), 2.75, 2.16, 2.06, 1.84 (3H each, CH$_3$ of L), 0.68 (t, J = 7.4 Hz, 3H, ≡CCH$_2$CH$_2$CH_3) (isomer ratio *ca.* 7 : 1). ^{13}C NMR (C_6D_6, 62.9 MHz): major isomer δ 250.0 (≡*C*Ph), 217.2 (≡*C*CH$_2$), 153.9, 153.2, 150.6, 144.7, 144.4, 144.2 (*C*Me of L), 139.6 (*ipso-C* of Ph), 130.8, 129.2 (Ph), 108.7, 108.3, 107.8 (*C*H of L), 86.9 (dd, J_{CH} = 103, 128 Hz, NbCH_2CH$_3$), 40.8 (t, J_{CH} = 127 Hz, ≡C*C*H$_2$), 22.4 (t, J_{CH} = 128 Hz, ≡CCH$_2$*C*H$_2$) 18.6, 15.9, 15.6, 14.8, 13.6, 13.3, 13.1 (NbCH$_2$*C*H$_3$, ≡CCH$_2$CH$_2$*C*H$_3$ and Me of L).

[NbL(Cl)(Et)(PhC≡CPh)] **2d**. ^{1}H NMR (C_6D_6, 200 MHz): δ 4.25 (dq, J = 12.6, 7.7 Hz, 1H, NbHC*H*CH$_3$), 1.10 (dd, J = 7.7, 6.0 Hz, 3H, NbCH$_2$CH_3), 0.47 (pseudo sxt, J = 12.5, 6.1 Hz, 1H, Nb*H*CHCH$_3$). ^{13}C NMR (C_6D_6, 50.3 MHz): δ 93.7 (dd, J_{CH} = 103, 128 Hz, NbCH_2CH$_3$).

[NbL(Cl)(Pr^n)(PhC≡CMe)] **3a**. ^{1}H NMR (C_6D_6, 250 MHz): major isomer δ 7.04–6.89 (m, 5H, Ph), 5.72, 5.53, 5.41 (1H each, CH of L), 3.69 (td, J = 12.2, 3.3 Hz, 1H, NbHC*H*CH$_2$CH$_3$), 3.68 (s, 3H, ≡CCH_3), 2.76, 2.21, 2.10, 2.08, 1.85, 1.53 (3H each, Me of L), 1.53 (m, 1H, NbCH$_2$CH_2CH$_3$), 0.86 (t, J = 6.9 Hz, 3H, NbCH$_2$CH$_2$CH_3), 0.71 (m, 1H, NbCH$_2$CH_2CH$_3$), 0.58 (m, 1H, Nb*H*CHCH$_2$CH$_3$); minor isomer (some resonances obscured) δ 8.22 (d, J = 7 Hz, 2H, *o-C* of Ph), 7.43 (t, J = 7.6 Hz, 2H, *m-H* of Ph), 7.21 (t, J = 7.6 Hz, 1H, *p-C* of Ph), 5.71, 5.59 (1H each, C*H* of L), 2.80, 2.51, 2.19, 2.07, 2.05, 1.77 (3H each, CH_3 of L or ≡CCH_3) (isomer ratio *ca.* 4 : 1). ^{13}C NMR (C_6D_6, 50.3 MHz): major isomer δ 249.7 (≡*C*Ph), 216.9 (≡*C*Me), 153.9, 153.4, 150.7, 144.7, 144.4, 144.2 (*C*Me of L), 139.7 (*ipso-C* of Ph), 130.6, 129.2 (Ph) 108.7, 108.2, 107.9 (CH of L), 95.9 (dd, J_{CH} = 106, 125 Hz, NbCH_2CH$_3$), 27.6 (t, J_{CH} = 127 Hz, NbCH$_2$CH_2CH$_3$), 23.4, 20.9, 15.9, 15.6, 14.7, 13.5, 13.3, 13.1 (NbCH$_2$CH$_2$*C*H$_3$, ≡C*C*H$_3$ and Me of L).

[NbL(Cl)(Pr^n)(PhC≡CEt)] **3b**. ^{1}H NMR (C_6D_6, 250 MHz): major isomer δ 3.88 (td, J = 12.2, 3.3 Hz, 1H, NbHC*H*CH$_2$CH$_3$), 1.52 (m, 1H, NbCH$_2$CH_2CH$_3$), 0.88 (t, J = 7.0 Hz, NbCH$_2$CH$_2$CH_3), 0.71 (m, 1H, NbCH$_2$CH_2CH$_3$), 0.60 (td, J = 12.0, 3.3 Hz, 1H, Nb*H*CHCH$_2$CH$_3$) (isomer ratio *ca.* 4 : 1). ^{13}C NMR (C_6D_6, 62.9 MHz): major isomer δ 95.7 (dd, J_{CH} = 108, 125 Hz, NbCH_2CH$_2$CH$_3$).

[NbL(Cl)(Me)(PhC≡CEt)] **4b**. ^{1}H NMR (C_6D_6, 200 MHz): major isomer δ 1.62 (s, 3H, NbMe) (isomer ratio *ca.* 7 : 1). ^{13}C NMR (C_6D_6, 50.3 MHz): major isomer δ 61.4 (q, J_{CH} = 122 Hz, NbMe).

[NbL(Cl)(Me)(PhC≡CPr^n)] **4c**. ^{1}H NMR (C_6D_6, 200 MHz): major isomer δ 7.05–6.86 (m, 5H, Ph), 5.75, 5.48, 5.46 (1H each, CH of L), 4.15 (m, 2H, ≡CCH_2CH$_2$CH$_3$), 2.42 (m, 2H, ≡CCH$_2$CH_2CH$_3$), 2.74, 2.23, 2.11, 2.10, 1.86, 1.80 (3H each, Me of L), 1.63 (s, 3H, NbMe), 1.24 (t, J = 7.2 Hz, 3H, ≡CCH$_2$CH$_2$CH_3); minor isomer (some resonances obscured) δ 8.20 (d, J = 7 Hz, 2H, *o-C* of Ph), 7.43 (t, 2H, *m-H* of Ph), 5.71, 5.59 (1H each, C*H* of L), 2.72, 2.07, 2.04 (3H each, Me of L), 0.67 (t, J = 7.4 Hz, 3H, ≡CCH$_2$CH$_2$CH_3) (isomer ratio *ca.* 7 : 1). ^{13}C NMR (C_6D_6, 50.3 MHz): major isomer δ 255.4 (≡*C*Ph), 222.8 (≡*C*CH$_2$), 153.7, 152.9, 151.1, 144.8, 144.3, 144.2 (*C*Me of L), 139.4 (*ipso-C* of Ph), 130.8, 129.2 (Ph), 108.8, 108.3, 108.1 (*C*H of L), 62.1 (q, J_{CH} = 123 Hz, NbMe), 41.2 (t, J_{CH} = 124 Hz, ≡*C*CH$_2$), 22.3 (t, J_{CH} = 128 Hz, ≡CCH$_2$*C*H$_2$) 16.1, 15.9, 15.6, 15.3, 13.6, 13.2, 13.1 (≡CCH$_2$CH$_2$*C*H$_3$ and Me of L).

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