Tetrahedron Letters, Vol. 34, No. 37, pp. 5875-5878, 1993
Printed in Great Britain

0040-4039/93 $6.00 + .00
Pergamon Press Ltd

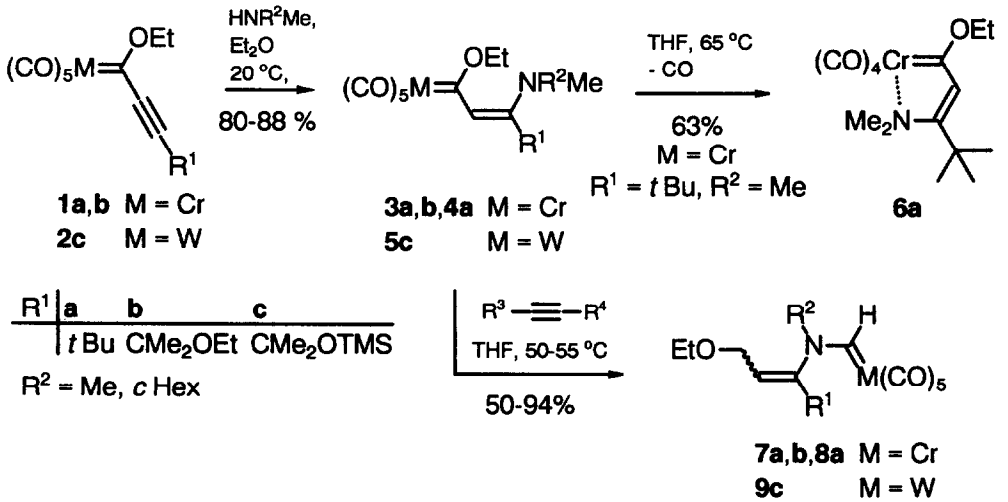
A Novel Rearrangement of the Carbene Ligand in (*Z*)-(2-Dialkylaminoethenyl)carbene Complexes

Michael Duetsch, Frank Stein and Armin de Meijere*

Institut für Organische Chemie der Georg-August-Universität Göttingen, Tammannstraße 2, D-37077 Göttingen, Germany

Abstract: (*Z*)-(2-Dialkylamino)carbenechromium and -tungsten complexes **3a,b,d,4a** and **5c**, which are readily available by Michael addition of secondary amines to alkynylcarbene complexes **1a,b,d** and **2c** rearrange to aminomethylene complexes **7a,b,d, 8a** and **9c**, when heated to 50–55 °C. **3a** yielded the chelated tetracarbonyl complex **6a** at 65 °C.

Phenyl- and ethenyl-carbene complexes of the Fischer type[1] attract most attention because of their cycloadditions with alkynes to give phenol and cyclohexadienone derivatives.[2] Amino substituents at C-2 of the ethenylcarbene ligand cause a total change in reactions of these complexes with alkynes. (*E*)-Configurated [(2-dimethylaminoethenyl)carbene]chromium complexes react with alkynes to yield cyclopentadienes,[3] whereas (*Z*)-configurated complexes with a bulky substituent at the ethenyl terminus react with two molecules of an alkyne to yield cyclopenta[*b*]pyrans.[4] [(*Z*)-(2-Alkylamino- and [(*Z*)-(2-aminoethenyl)carbene]chromium complexes cycloadd alkynes to give 4(1*H*)pyridinylidene complexes and pyridines, respectively.[5] Chromium coordinated 1-aza-1,3-butadienes were obtained upon simple heating of the latter complexes with primary amino groups.[5,6] We here report about the unprecedented thermal rearrangement of [(*Z*)-(2-dialkylaminoethenyl)carben]chromium and tungsten complexes.



Scheme 1. (Details see Table 1)

The (*Z*)-(2-dialkylaminoethenyl)carbene complexes **3a,b**, **4a** and **5c** are readily available in high yields by Michael addition of secondary amines to alkynylcarbene complexes **1a,b** and **2c**.[7-11] The *tert*-butyl derivative **3a** lost one carbonyl ligand when heated to 65 °C in tetrahydrofuran to yield the chelated tetracarbonyl complex **6a**, as had been shown for similar complexes before.[8,11] However, such dark brown complexes were not observed, when (*Z*)-configurated [(2-dialkylaminoethenyl)carbene]chromium and tungsten complexes **3a,b**, **4a** and **5c** were cautiously heated to 50–55 °C in THF solution. A very slow reaction took place instead: After eight days, only 83% of **3a** had been converted and a light yellow compound was isolated. The product consisted of two isomers, which could not be separated by column chromatography. Mass and IR spectra of the product indicated that a rearrangement to a new pentacarbonylchromium complex had taken place. The constitution of the product as the aminomethylenechromium complex **7a** was established on the basis of its ^{1}H NMR (singlet at δ = 10.6 ppm and a H_A, H_B, H_M-system) and DEPT ^{13}C NMR spectra (positive signal at δ = 270 ppm).[11] The conversion of **3a** to **7a** was accelerated in the presence of a non-terminal alkyne (entries 2 and 3 in Table 1).

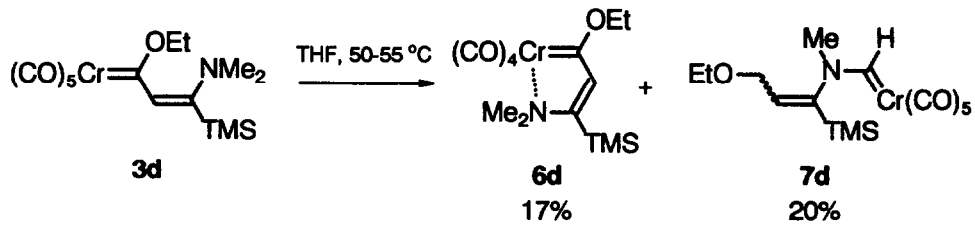
This novel rearrangement of a carbene ligand is not restricted to **3a**. The dimethylamino compound **3b** and the *N*-cyclohexyl-*N*-methylamino derivative **4a** underwent the same reaction (Scheme 1, entries 4 and 6 in Table 1). The tungsten derivative **5c** rearranged much more easily. The corresponding product **9c** was obtained in 94% yield even in the absence of any disubstituted alkyne (entry 7 in Table 1). In addition, terminal alkynes did not insert into the metal carbene bond of **5c** to yield cyclopenta[*b*]pyrans, as it was observed for the chromium counterparts.[4] In the presence of 1-pentyne or phenylacetylene, **9c** was isolated, albeit in lower yield (entries 8 and 9 in Table 1). It is noteworthy, that with an added 1-alkyne, the ratio of (*E*)-and (*Z*)- isomers of **9c** changed completely from 5 : 1 to 0.5 : 1.

A prerequisite for this rearrangement appears to be the (*Z*)-configuration of the starting complex, because it has never been observed with any (*E*)-configurated (2-dialkylaminoethenyl)carbene complex. (*Z*)-Configuration is only realized in (2-dialkylaminoethenyl)carbene complexes, when a bulky tertiary substituent is attached at the terminus of the starting ethynyl substituted complex.[8]

Table 1. Rearrangement of (*Z*)-(2-dialkylaminoethenyl)carbene complexes **3a,b,d**, **4a** and **5c** to aminomethylene complexes **7a,b,d**, **8a** and **9c** in tetrahydrofuran at 50–55 °C.[11]

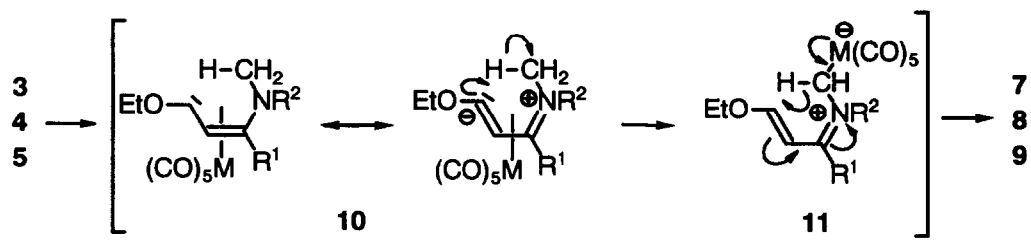
Entry	Starting material	M	R^1	R^2	Alkyne R^3, R^4	time [d]	Product	Yield (%)	Ratio of isomers
1	**3a**[8]	Cr	*t* Bu	Me	–	8σ	**7a**	50[a]	13 : 1
2	**3a**[8]	Cr	*t* Bu	Me	Et, Me	4	**7a**	59	13 : 1
3	**3a**[8]	Cr	*t* Bu	Me	Ph, Ph	4	**7a**	51	13 : 1
4	**3b**[8]	Cr	CMe_2OEt	Me	Et, Me	4	**7b**	54	5 : 1
5	**3d**[8,12]	Cr	TMS	Me	–	5	**7d**	20[b]	9 : 1
6	**4a**[9]	Cr	*t* Bu	*c* Hex	Et, Me	4	**8a**	74	19 : 1
7	**5c**	W	CMe_2OTMS	Me	–	5	**9c**	94	5 : 1
8	**5c**	W	CMe_2OTMS	Me	*n* Pr, H	4	**9c**	52[c]	0.5 : 1
9	**5c**	W	CMe_2OTMS	Me	Ph, H	4	**9c**	71[d]	0.5 : 1

[a] In addition, 17% of the starting material **3a** were recovered. – [b] In addition 17% of the chelated tetracarbonyl complex **6d** were isolated. – [c] In addition, 40% of the starting material **5c** were recovered. – [d] In addition, 13% of the starting material **5c** were recovered.



Scheme 2

The trimethylsilyl substituted complex **3d**,[8,12] when heated to 50-55 °C in tetrahydrofuran, gave a mixture of the chelated tetracarbonylchromium complex **6d** and the aminomethylene complex **7d** in poor yield only. This product **7d**, like **7a,b**, **8a** and **9c**, is obtained as a mixture of two isomers, which probably differ in the configuration of the C,C-double bond.



Scheme 3. A possible mechanism for the formation of **7a,b,d**, **8a** and **9c**.

The mechanism of this rearrangement can only be speculated about (Scheme 3). An initial release of the carbene ligand could lead to a coordinated ethenylcarbene of type **10**. As a consequence of the γ-amino group, this ethenylcarbene ought to be rather nucleophilic and an unusual proton shift could take place to form the σ-alkyl complex **11**. A subsequent [1,5]-hydride shift would then lead to the product. This mechanism is consistent with the observation that only (*Z*)-configurated complexes rearrange in this fashion, but the effect of added alkynes in accelerating this rearrangement is not at all understood.

Acknowledgements: This work was supported by the Volkswagen-Stiftung and the Fonds der Chemischen Industrie as well as Hoechst AG and Hüls AG through generous gifts of chemicals. M. D. is grateful to the Deutsche Forschungsgemeinschaft, "Graduierten-Kolleg: Kinetik und Selektivität chemischer Prozesse in verdichteter fluider Phase" for a graduate fellowship.

References and Notes

1. For a recent review see: W. D. Wulff in *Comprehensive Organic Synthesis*, B. M. Trost, I. Fleming, Eds., Vol. 5, Pergamon, Oxford, **1991**, pp. 1065–1113.
2. (a) K. H. Dötz, *Angew. Chem.* **1975**, *87*, 672–673; *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 644. – (b) K. H. Dötz, R. Dietz, A. von Imhof, H. Lorenz, G. Huttner, *Chem. Ber.* **1976**, *109*, 2033–2038. – (c) P.-C. Tang, W. D. Wulff, *J. Am. Chem. Soc.* **1984**, *106*, 1132–1135.
3. (a) M. Duetsch, R. Lackmann, F. Stein, A. de Meijere, *Synlett*, **1991**, 324–326. – (b) R. Aumann, H. Heinen, M. Dartmann, B. Krebs, *Chem. Ber.* **1991**, *124*, 1229–1236.
4. F. Stein, M. Duetsch, R. Lackmann, M. Noltemeyer, A. de Meijere, *Angew. Chem.* **1991**, *103*, 1669–1671; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1658–1660.
5. (a) R. Aumann, P. Hinterding, *Chem. Ber.* **1992**, *125*, 2765–2772. – (b) M. Duetsch, F. Stein, F. Funke, E. Pohl, R. Herbst-Irmer, A. de Meijere, *Chem. Ber.*, submitted for publication.
6. R. Aumann, P. Hinterding, *Chem. Ber.* **1990**, *123*, 2047–2051.
7. E. O. Fischer, H. J. Kalder, *J. Organomet. Chem.* **1977**, *131*, 57–64.
8. M. Duetsch, F. Stein, R. Lackmann, E. Pohl, R. Herbst-Irmer, A. de Meijere, *Chem. Ber.* **1992**, *125*, 2051–2065.
9. *N*-Cyclohexyl-*N*-methylamine was added to **1a** at –78 °C to avoid the formation of the corresponding allenylidenechromium complex.[10]
10. F. Stein, M. Duetsch, E. Pohl, R. Herbst-Irmer, A. de Meijere, *Organomet.* **1993**, *12*, in press.
11. All new compounds were fully characterized by spectroscopic techniques (^{1}H NMR, ^{13}C NMR, IR, MS) and their molecular formulas in general established by microanalysis or high resolution mass spectrometry. ^{1}H NMR (250 MHz, C_6D_6) and ^{13}C NMR (62.89 MHz, C_6D_6, add. DEPT) data for representative compounds are as follows: **6a**: δ = 0.76 [s, 9 H, $C(CH_3)_3$], 1.29 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.62 [s, 6 H, $N(CH_3)_2$], 4.92 (q, ^3J = 7.0 Hz, 2 H, OCH_2), 5.95 (s, 1 H, 2-H); 15.11 (+, OCH_2CH_3), 31.95 [+, $C(CH_3)_3$], 38.70 [C_{quat}, $C(CH_3)_3$], 55.06 [+, $N(CH_3)_2$], 76.74 (–, OCH_2), 135.29 (+, C-2), 182.35 (C_{quat}, C-3), 217.86, 231.27, 233.70 (C_{quat}, C=O), 338.33 (C_{quat}, C-1). – **7a**: δ = 1.05 [s, 9 H, $C(CH_3)_3$], 1.15 (t, ^3J = 7.2 Hz, 3 H, OCH_2CH_3), 2.49 (s, 3 H, NCH_3), 3.31 (q, ^3J = 7.2 Hz, 2 H, OCH_2), 3.75 (dd, ^3J = 8.4, ^2J = 12.2 Hz, 1 H, $CHCH_2OCH_2$), 3.95 (dd, ^3J = 4.6, ^2J = 12.2 Hz, 1 H, $CHCH_2OCH_2$), 5.73 (dd, ^3J = 8.4, ^3J = 4.6 Hz, 1 H, $CHCH_2OCH_2CH_3$), 10.64 (s, 1 H, Cr=CH); 15.29 (+, OCH_2CH_3), 30.66 [+, $C(CH_3)_3$], 35.28 [C_{quat}, $C(CH_3)_3$], 56.14 (+, NCH_3), 66.57, 66.90 (–, OCH_2), 124.33 (+, C-2), 154.08 (C_{quat}, C-3), 217.90, 223.57 (C_{quat}, C=O), 269.92 (+, Cr=CH).
12. A. Rahm, W. D. Wulff, *Organomet.* **1993**, *12*, 597–599.

(Received in Germany 21 June 1993; accepted 5 July 1993)