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Preliminary Communication

1,3-Dipolar cycloaddition reactions of alkenylalkoxycarbene chromium complexes

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Abstract

New spiropyrazoline derivatives from the 1,3-dipolar cycloaddition of diazomethane to alkenylalkoxycarbene complexes are isolated and fully characterized as $Cr(CO)_5$ complexes. Me_3SiCHN_2 reacts selectively with the C–C double bond to give new pentacarbonylchromium carbene complexes.

Key words: Chromium; Carbene; 1,3-Dipolar addition

The α,β-unsaturated Fischer-type transition metal–carbene complexes have been widely used as dienophiles in both Diels–Alder reactions [1] and benzannulation reactions with alkynes [2]. In the case of Diels–Alder reactions, alkenylalkoxycarbene complexes behave as powerful dienophiles with extraordinary reaction rates and *exo/endo* selectivities, comparable with those of the Lewis acid catalyzed Diels–Alder reaction of α,β-unsaturated esters [1]. Although the carbon–carbon double bond in these complexes is expected to be reactive in 1,3-dipolar cycloaddition, to our knowledge there have been no reports concerning their reactivity towards 1,3 dipoles. The only reported 1,3-dipolar cycloaddition reaction concerned the reactivity of alkoxyalkynylcarbene complexes to diazoalkanes [3,4]. There are two possible reactive sites for these complexes, the carbon–carbon triple bond where the cycloaddition takes place and the metal–carbon double bond which is transformed into a carbon–carbon double bond. In addition, it is impossible to discriminate between these two sites using diazomethane [3] and a mixture of the two pyrazole derivatives **2** and **3** is always obtained starting from complex **1**. In contrast, selective cycloaddition to the triple bond has been performed using the more sterically hindered trimethylsilyldiazomethane, giving only compounds **2** [4].

In this last case, trimethylsilyldiazomethane acts as a synthetic equivalent of diazomethane, since the silyl group in the cycloaddition product is lost during work-up (Scheme 1).

We have recently reported that pentacarbonyl(2-oxacyclopentylidene)chromium(0) complexes are easily transformed into the corresponding *exo*-methylene derivatives **4** by the reaction of their conjugate bases with Eschenmoser's salt [5].

In this preliminary communication, we report the reaction of complexes **4** with diazoalkanes. As expected, the *exo*-methylene derivatives **4a–c** react with an excess of diazomethane to give the interesting spiropyrazolines **5a–c** (Scheme 2). The reaction is carried out by mixing (under argon) a diethyl ether solution of diazomethane (generated by adding 1.5 ml of 10 M NaOH to 4 mmol of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide dissolved in 20 ml of a 1:1 solution of diethyl ether and methoxyethanol) with a dichloromethane or diethyl ether solution (20 ml) of **4a–c** (1 mmol) cooled to −5°C. The reaction is very fast, and the starting material is consumed within 10 min. The evaporation of solvent under reduced pressure gives a crude material from which the spiropyrazolines are recovered in the form of their pentacarbonylchromium complexes **5a–c** by means of column chromatography. The exposure of an etheral solution of **5b** to air and sunlight for 48 h affords **6** as a white solid, in 74% yield after chromatographic purification.

Analytical and spectroscopic data are consistent with the structures proposed for **5a–c** and **6** [6].

The presence of the *exo*-methylene double bond in the cycloaddition products **5a–c** clearly shows that the reaction is not chemoselective and that diazomethane reacts with both the carbon–carbon and carbon–metal double bond [3]. With the aim of producing $Cr(CO)_5$ carbene complex derivatives, it was decided to treat **4a** with trimethylsilyldiazomethane which, because of its steric requirements, was expected to exhibit selectivity for the *exo* carbon–carbon double bond [4]. The reac-

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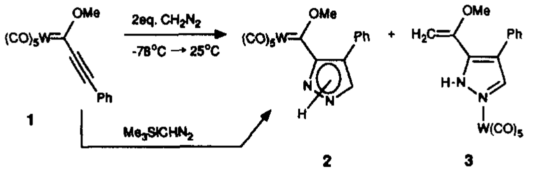


Scheme 1.

tion was carried out by heating **4a** with Me_3SiCHN_2 at 68°C for 8 h in hexane. The spiropyrazoline derivative **7** was obtained in 52% yield as a mixture of three diastereoisomers which could not be separated [6] (Scheme 3).

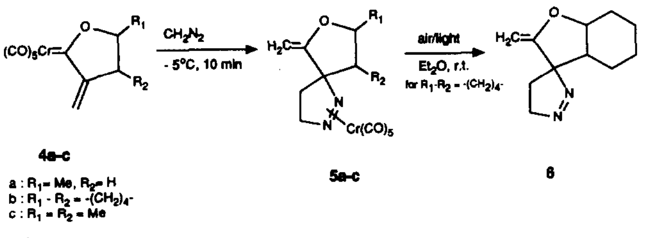
In analogy with the behaviour of alkynylcarbene complexes, the reactions of alkenylcarbene complexes **3** with diazoalkanes seem to be regioselective (although the yields are not so high), and the formation of the C–C bond occurs at the β-carbon atom of *exo*-methylene double bond.

In an attempt to elucidate the origin of the regioselectivity, the spectroscopic data were analyzed for signs of alkenylalkoxycarbene complexes.

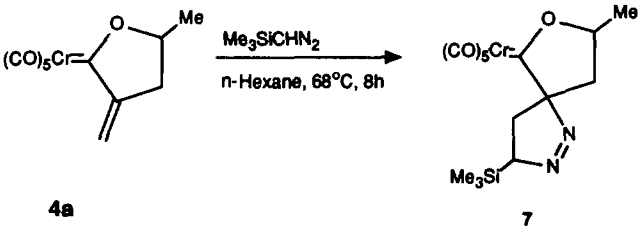
It has already been reported [7] that the β-vinyl carbon atom in complex **8** shows high field absorption, whereas the resonance frequency of the α-carbon atom is shifted downfield (Fig. 1). This would suggest that the resonance effects involving the $Cr(CO)_5$ group are not important, and that it is the inductive effect of the $Cr(CO)_5$ group which is responsible for the observed downfield shift of the α carbon in the alkenyl function. These data are consistent with a preferred conformation in which the p orbitals of the vinyl group and the carbon–metal double bond cannot interact [8].

The difference between the ^{13}C NMR chemical shifts of α and β vinyl carbons is also considerable in our compounds, the α-carbon always being shifted downfield (Fig. 1).

The charge distribution on the *exo*-methylene bond of complexes **4a–c** that might be inferred from the ^{13}C NMR data does not fit with the regioselectivity found in the reactions with diazoalkanes. It is likely that factors other than electronic interactions are operating.



Scheme 2.



Scheme 3.

For example, the frontier orbital control may be governing our reaction, as happens in the case of the HOMO dipole-controlled cycloaddition reaction of CH_2N_2 to methylacrylate, which shows the same regioselectivity as we found when CH_2N_2 was added to α,β-alkenylcarbene complexes. Unfortunately, there are no calculations concerning the orbital energies and coefficients of alkenylcarbene complexes to give theoretical support to this interpretation of our experimental results.

In conclusion, this article describes the first example of a 1,3-dipolar cycloaddition reaction to alkenylalkoxycarbene complexes, which also represents interesting access to 3,3′-*spiro*-(2-methylene-tetrahydrofuran)(1′-pyrazoline) **5** and to pentacarbonyl[3,3′-*spiro*-(5-methyl-2-oxacyclopentylidene)(5-trimethylsilyl-1-pyrazoline)]-chromium(0) complex **7**. We have shown that the 1,3-dipolar cycloaddition reaction can be performed regioselectively on pentacarbonyl(5-methylene-2-oxacyclopentylidene)chromium complexes **4**, and that chemoselectivity can be achieved by using Me_3SiCHN_2 as the diazoalkane.

We intend to further our investigation into the behaviour of complexes **4** by using other 1,3-dipoles.

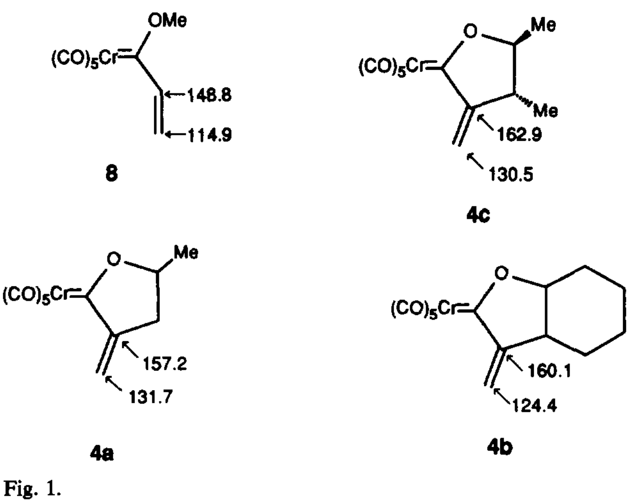


Fig. 1.

Acknowledgements

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6 All of the isolated new **5a–c** compounds have been characterised by means of elemental analyses, IR, ^{1}H NMR spectroscopy and mass spectroscopy. *Selected physical and spectroscopic data for*: **5b**: yield 42%, m.p. 145°C (dec.); IR (Nujol) cm^{-1}: 2060 (ν CO$_{trans}$), 1980–1860 (ν CO$_{cis}$), 1655 (ν C=C); ^{1}H-NMR (CDCl$_3$, 200 MHz) δ ppm: 1.00–2.40 (m, 11H, -CH- and -CH$_2$- cyclohexyl, -CH$_2$- pyrazoline), 3.82 [d, 1H, $J_{gem}=3$ Hz, O-C=C(H)H$_{trans}$], 4.35 (m, 1H, -O-CH- cyclohexyl), 4.52 [d, $J_{gem}=$ 3 Hz, -O-C=C(H)H$_{cis}$], 4.57 (m, 2H, -CH$_2$N$_2$-); ^{13}C-NMR (CDCl$_3$, 200 MHz) δ ppm: 221.74 (s, CO$_{trans}$), 214.89 (s, CO$_{cis}$), 162.81 (s, H$_2$C=*C*), 98.84 (s, -H$_2$C-*C*-N$_2$-), 84.85 (t, H$_2$*C*=C), 83.49 (d, -O-CH-), 83.31 (t, -CH$_2$-*C*H$_2$-N$_2$-), 55.92 (t, -*C*H-CH$_2$-), 31.74, 27.94, 25.93, 24.38, 23.34 (5t, -(CH$_2$)$_4$- cyclohexyl and -*C*H$_2$-CH$_2$-N$_2$-); MS (EI) m/z 384 (M$^+$). Elemental analysis. Found: C, 49.96; H, 4.39; N, 7.08. $C_{16}H_{16}N_2O_6Cr$, calcd. C, 50.00; H, 4.17; N, 7.24.
6: yield 74%, m.p. 79°C (pentane −78°C); IR (Nujol) cm^{-1}: 1650 (ν C=C); ^{1}H-NMR (CDCl$_3$, 200 MHz) δ ppm: 1.00–2.40 (m, 11H, -CH- and -CH$_2$- cyclohexyl, -CH$_2$- pyrazoline), 3.78 [d, 1H, $J_{gem}=3$ Hz, -O-C=C(H)H$_{trans}$], 4.15 [d, $J_{gem}=3$ Hz, -O-C=C(H)H$_{cis}$], 4.20–4.57 (m, 3H, -CH$_2$N$_2$- and -O-CH-).
7: yield 52%, mixture of three diastereoisomers; ratio by ^{1}H-NMR 48:30:22), oil; IR (neat) cm^{-1}: 2065 (ν CO$_{trans}$), 1995–1895 (ν CO$_{cis}$), 1450 (ν N=N); ^{1}H-NMR (CDCl$_3$, 300 MHz) δ ppm: 0.10, 0.12, 0.13 (3s, 9H, Me$_3$Si–, three diastereoisomers), 0.35 (t, 1H, $J_{vic}=10$ Hz, Me$_3$Si-C*H*–, one diastereoisomer), 1.55, 1.61, 1.63 (3d, 3H, $J_{vic}=6.4$ Hz, -O-CH-C*H*$_3$, three diastereoisomers), 1.15–2.33 (m, 5H, Me$_3$Si-CH-C*H*$_2$–, -O-CH-C*H*$_2$- three diastereoisomers and Me$_3$Si-C*H*-CH$_2$- two diastereoisomers), 4.82, 5.09, 5.25 (3m, 1H, -O-CH- three diastereoisomers); ^{13}C-NMR (CDCl$_3$, 300 MHz) δ ppm: 342.3, 336.0, 335.4 (3s, C=Cr, three diast.), 223.0, 222.6 (2s, CO$_{trans}$, three diast.), 216.9, 216.5 (2s, CO$_{cis}$, three diast.), 92.0, 90.0 (2d, -O-CH-, three diast.), 57.7, 56.1, 55.3 (3t, -CH$_2$-*C*-N$_2$–, three diast.), 43.9, 35.8, 34.6 (3t, -O-CH-*C*H$_2$–, three diast.), 24.5, 20.9, 19.9, 19.7, 19.6, 19.4 (Me$_3$Si-*C*H-CH$_2$- and Me$_3$Si-CH-*C*H$_2$- three diast.), −1.6, −1.5, −1.3 [(CH$_3$)$_3$Si-three diast.].

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