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Chromium – Copper Exchange of Fischer Carbene Complexes: X-Ray Crystal Structure of a [Cu{=CR¹(OR²)}(MeCN)(Et₂O)][PF₆] Complex**

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Over the last two decades Fischer-type carbene complexes have become valuable tools in stoichiometric transition metal mediated organic synthesis.^[1] The carbene nature of these complexes is demonstrated by their ability to transfer the carbene ligand not only to alkenes (cyclopropanation),^[2] but also to oxygen, nitrogen, and carbon through the corresponding ylides (amine oxides and dimethyl sulfoxide; sulfilimines; P-C, S-C, and N₂-C ylides).^[3] Although transmetalation is probably the most important single process in organometallic chemistry, particularly for transition metal catalyzed reactions,^[4] the simple transfer of a carbene ligand from a metalcarbene complex to another metallic center is rare.^[5] Carbene complexes of Rh, Pd, Pt, Cu, and Ag have been formed by transfer of diaminocarbene ligands (imidazolinylidene or imidazolidinylidene ligands, which are found to be readily transferred between metal centers) from Group 6 metal carbene complexes.^[5-7] However, the transfer of alkoxycarbene ligands has been reported only for [Mo{=CPh(OMe)}-(CO)(Cp)(NO) to $[Fe(CO)_5]^{[8]}$ and $[W{=CPh(OMe)}(CO)_5]$ to H[AuCl₄].^[9] Very recently Sierra et al. have proposed palladium biscarbene complexes as the active intermediates in the palladium-catalyzed dimerization of alkoxycarbenechromium complexes.[10, 11]

In the context of our studies on copper-catalyzed coupling reactions of Fischer carbene complexes we report here on 1) the cross-coupling of Fischer chromium – carbene complexes with ethyl diazoacetate (EDA), and 2) the isolation and full characterization of the first alkoxycarbene complex of copper(I). A recent, excellent report by Hofmann and Straub^[12] on the characterization of an alkoxycarbonylcarbene – copper complex has prompted us to release our results.

When chromium-carbene complexes 1 were treated with EDA (2.5 equiv) and CuBr (15% mol) in THF at room temperature the alkenes 2 were isolated with high yields (80-95%) along with ethyl maleate and ethyl fumarate

- [+] X-ray crystal structure analysis.
- [**] This work was supported by DGICYT (PB97-1271) and CICYT (BQU2000-0219). O.L. thanks the Fonds der Chemischen Industrie for a postdoctoral fellowship.
- Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

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(Scheme 1). This heterocoupling reaction worked well for phenyl- (1a), butyl- (1b) and alkenyl(methoxy)carbene (1c) complexes, as well as for the nonracemic alkenyl(menthoxy)-carbene 1d, giving rise to alkenes and dienes with a high degree of functionality.^[13] The methoxy complexes 1a-c afforded a 1:1 E/Z mixture, whereas only the E stereoisomer was formed in the case of the menthoxy derivative 1d.



Scheme 1. CuBr-catalyzed cross-coupling reaction of alkoxychromium carbene complexes **1** with ethyl diazoacetate (**a**: $R^1 = Ph$, $R^2 = Me$; **b**: $R^1 = Bu$, $R^2 = Me$; **c**: $R^1 = (E)$ -CH=CH-2-furyl, $R^2 = Me$; **d**: $R^1 = (E)$ -CH=CH-2-furyl, $R^2 = (1R,2S,5R)$ -menthyl): a) 15 mol % CuBr, THF, 25 °C, 80 – 95 %; E:Z = 1:1 ($R^2 = Me$), > 30:1 ($R^2 = (1R,2S,5R)$ -menthyl).

On the other hand, when the (methoxy)carbene **1c** was stirred with 15 mol% [Cu(MeCN)₄][PF₆] in the absence, or even in the presence, of EDA and under homogeneous conditions (CH₂Cl₂, 25 °C) a clean dimerization to triene **3a** took place (95% yield; E/Z = 10:1; Scheme 2). On the basis of



Scheme 2. Formation of the copper-carbene complex **5** from **1d** and $[Cu(MeCN)_4][PF_6]$ (**3a**: $R^1 = (E)$ -CH=CH-2-furyl, $R^2 = Me$; **3b**, **4**, **5**: $R^1 = (E)$ -CH=CH-2-furyl, $R^2 = (1R,2S,5R)$ -menthyl): a) 15 mol% [Cu(MeCN)_4][PF_6], CH_2Cl_2, 25°C, 95%; b) 50 mol% [Cu(MeCN)_4][PF_6], CH_2Cl_2, 25°C; c) crystallization from CH_2Cl_2/Et_2O (1/5, v/v), -20°C, 50% (35% recovery of **1d**).

previous work^[5, 10] we assume that a copper biscarbene species of the type $[Cu{=}CR^{1}(OMe)]_{2}L_{n}][PF_{6}]$ might be the real metal intermediate. At this point, it was gratifying to find that the homochiral (menthoxy)carbene complex 1d consumed 0.5 equivalents of [Cu(MeCN)₄][PF₆] (CH₂Cl₂, 25 °C) yielding a clean crude mixture consisting of $[Cr(CO)_5(MeCN)]$ (identified by comparison with an authentic sample) and a copper-carbene complex, presumably of structure 4 (Scheme 2). The structure 4 is proposed on the basis of the single set of signals in the ¹³C NMR spectrum ($\delta = 280$ (Cu=C), 4.1 (Cu-NC-CH₃)).^[14] Surprisingly, when the crude mixture was dissolved in CH₂Cl₂ and Et₂O (1/5, v/v) was allowed to diffuse into the brown solution the color slowly changed to reddish and orange crystals of the new complex 5 deposited at -20° C (50% yield with respect to the starting copper complex). The starting carbene complex 1d could be recovered from this solution (ca. 35% after chromatographic

purification, 70% based on the conversion). This process implies two unprecedented events on the coordination sphere of copper, 1) exchange of the carbene ligand for a diethyl ether ligand, and 2) transfer of the carbene ligand back to the chromium atom.

The structure of **5** was confirmed by a single-crystal X-ray structure analysis (Figure 1), ^[15] which shows that the copper atom is three-coordinate, bonded to the carbene carbon atom



Figure 1. The structure of **5** (ORTEP view). For clarity, the hexafluorophosphate ion and hydrogen atoms are omitted. Thermal ellipsoids are drawn at 30% probability. Selected distances [Å] and angles [°]: Cu-C1 1.882(3), Cu-N 1.891(3), Cu-O2 2.345(2), C1-Cu-N 150.88(14), C1-Cu-O2 114.22(12), N-Cu-O2 94.90(11), N-Cu-C1-C2 -69.4(4), O2-Cu-C1-C2 112.5(3), Cu-C1-C2-C3 4.5(5).

(C1), the diethyl ether oxygen atom (O2), and the acetonitrile nitrogen atom (N) in an approximately trigonal fashion. The planes defined by O2, N, C1, Cu (mean deviation: 0.0050 Å) and Cu, O1, C2, C1 (mean deviation: 0.0003 Å) deviates from an orthogonal arrangement; the N-Cu-C1-C2 and O2-Cu-C1-C2 torsion angles are -69.4° and 112.5°, respectively. The alkenyl and copper carbene moieties are coplanar (Cu-C1-C2-C3 torsion angle: 4.5°). The Cu-C(carbene) distance (1.882 Å) is in agreement with that reported for X-Cu=CR₂ complexes.^[16] The Cu-C2 (2.96 Å) and Cu-C3 (3.24 Å) distances rule out a possible copper-alkene coordination.^[17]

Complex **5** is stable in the solid state or in solution (CH₂Cl₂, toluene) for several days at -20 °C under nitrogen. The ¹H, ¹³C, ³¹P, and ¹⁹F NMR spectra were recorded in CD₂Cl₂ at ambient temperature without decomposition. The Cu=C carbon atom resonates at $\delta = 276.5$.^[18] Despite the creation of a chirality axis, a single set of signals was observed in the variable-temperature ¹H NMR spectra between -80 °C and 25 °C. The UV spectrum of **5** ($\lambda_{max} = 383$ nm, $\varepsilon = 42300$, in CH₂Cl₂) suggests a $\pi - \pi^*$ transition of the copper–carbon double bond with predominant metal-to-ligand charge-transfer character.

The carbene ligand of both complexes **4** and **5** dimerized stereoselectively in the presence of tributylphosphane

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(3 equiv, CH₂Cl₂, 25 °C) affording the (1*E*,3*E*,5*E*)-1,3,5-triene **3b** (75% for **4**; 82% for **5**). Moreover, we found that the copper complex **5** catalyzed the dimerization of EDA (CH₂Cl₂, 25 °C) to a mixture of ethyl maleate and ethyl fumarate, with retention of the structural integrity of the catalyst.

In summary, chromium-carbene complexes efficiently transfer the carbene ligand to a copper(I) center allowing the preparation of functionalized alkenes, dienes, and trienes through homo- and heterocoupling reactions. A new copper(I)-carbene complex has been isolated and structurally characterized by X-ray diffraction that features, 1) an uncommon tricoordinate pattern, and 2) the presence of two other ligands with fair (MeCN) and very low (Et₂O) coordination capability. It should be emphasized that no X-ray structural determination has been hitherto achieved for copper(I) carbene complexes of the type $[ML_3]$,^[17] rather only the spectroscopic characterization has been reported for a few d¹⁰ copper carbene complexes containing either highly donor carbene ligands (tert-butyl-substituted imidazoline and imidazolidine carbenes)^[5-7] or extremely basic, sterically demanding iminophosphanamide ligands.^[12] Further work directed to study the potential of these chiral copper(I)-carbene complexes in asymmetric catalysis is in progress.

Received: May 10, 2001 [Z17084]

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HMBC experiments clearly indicate correlation between the olefinic C_{β} hydrogen atom and the carbone carbon atom.

- [15] Crystal structure data for 5. $C_{23}H_{37}CuF_6NO_3P$: $M_r = 584.05$, orange plates, dimensions = $0.45 \times 0.20 \times 0.10$ mm, orthorhombic, space group $P2_12_12_1$ (determined from the systematic absences), a =7.3757(1), b = 14.2948(2), c = 26.6661(3) Å, V = 2811.52(6) Å³, $\lambda =$ 1.5418 Å, Z = 4, $\rho_{\text{calcd}} = 1.380 \text{ Mg m}^{-3}$, F(000) = 1216, $\mu(\text{Cu}_{\text{K}\alpha}) =$ 2.207 mm⁻¹. The crystals are extremely air-sensitive. The sample was mounted in an appropriately sized cryoloop, and it was completely covered with mineral oil to prevent it from being in contact with oxygen. The crystal was held at 120(2) K with an Oxford Cryosystems Cryostream Cooler. Data collection was performed on a Nonius KappaCCD single-crystal diffractometer (fine-focus sealed tube, horizontally mounted graphite crystal, 95 mm CCD camera). The crystal-detector distance was fixed at 29 mm, and a total of 1018 images were collected by using the oscillation method (φ and ω scans), with 1° oscillation and 30 s exposure time per image. The data collection strategy was calculated with the program COLLECT. Data reduction and cell refinement were performed with the programs HKL DENZO and SCALEPACK. Unit cell dimensions were determined from 30381 reflections between $\theta = 1.473^{\circ}$ and 70.076°. A total of 20320 reflections were measured ($\theta_{\min} = 3.51^\circ, \theta_{\max} = 69.79^\circ$; $-8 \le h \le 8$, $0 \le k \le 17$, $0 \le l \le 32$). Multiple observations were averaged ($R_{int} = 0.059$), resulting in 5197 unique reflections of which 4910 were observed with $I > 2\sigma(I)$. Final mosaicity was 0.616(1)°. All data completeness was 98.7%. Intensity-error ratio for all reflections was 413.0:17.6. The crystal structure was solved by Patterson methods and phase expansion using the program DIRDIF-99.2. An empirical absorption correction was applied $(T_{\min} = 0.450; T_{\max} = 1.000)$ using XABS2. Anisotropic least-squares refinement was carried out with SHELXL-97. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were geometrically placed riding on their parent atoms with isotropic displacement parameters set to 1.2 times the $U_{\rm eq}$ value of the atoms to which they are attached (1.5 for methyl groups). The final cycle of full-matrix least-squares refinement based on 5197 reflections and 317 parameters converged to a final value of R1(observed) = 0.0405, R1(all data) = 0.0445, wR2(all data) = 0.1024, S = 1.083, $(\Delta/\sigma)_{\text{max}} = 0.003$, weighting scheme $w = 1/[\sigma^2(F_o^2) +$ $(0.0000 P)^2 + 2.6320 P$, where $P = (F_0^2 + 2F_c^2)/3$. Final difference Fourier maps showed no peaks higher than 0.366 e Å $^{-3}$ nor deeper than $-0.288 \text{ e} \text{Å}^{-3}$. Flack parameter = 0.00(3). Geometrical calculations were made with PARST97. The crystallographic plots were made with PLATON. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-163238. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam. ac.uk).
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1433-7851/01/4018-3394 \$ 17.50+.50/0 Angew. Chem. Int. Ed. 2001, 40, No. 18