Chromium(0)−Carbene Complexes as Carbene Sources: Self-Dimerization and Inter- and Intramolecular C−H Insertion Reactions Catalyzed by Pd(OAc)$_2$

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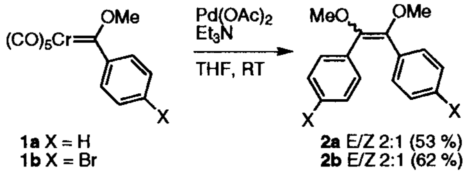
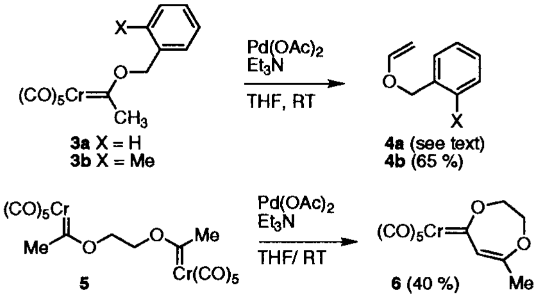
The role of heteroatom-stabilized group 6 metal−carbene complexes as stable carbene sources has been extensively investigated.[1] In fact, the cyclopropanation of olefins was one of the earliest reactions reported for Fischer-type carbene complexes.[2] On the other hand, thermal decomposition ($T > 130$ °C) of carbene complexes leads to carbene dimers. The *E/Z* ratio of the olefinic products is metal dependent, which excludes the participation of free carbenes in at least some of these processes.[3] C−H insertion processes have also been reported for group 6 Fischer−carbene complexes.[4] Apart from intramolecular cyclopropanation reactions,[5] which take place at room temperature or below, the carbene transfer from heteroatom-stabilized group 6 metal−carbene complexes usually needs temperatures over 80 °C to occur. We report here that dimerization and intramolecular C−H insertion reactions of alkoxychromium(0) carbenes can be effected at room temperature or below, in the presence of catalytic amounts of Pd(OAc)$_2$, and that the formal insertion of aminochromium(0) carbenes into olefinic C−H bonds is also catalyzed by Pd(OAc)$_2$.

The first assays to determine the viability of metal-catalyzed carbene transfer from group 6 stabilized metal−carbene complexes were carried out by reacting pentacarbonyl[(methoxy)(phenyl)carbene]chromium(0) (**1a**) and catalytic amounts of Rh$_2$(OAc)$_4$ at different temperatures.[6] We observed that self-dimerization of complex **1a** occurred at temperatures around 100 °C, high enough to not be clearly advantageous over the uncatalyzed process. We then turned our attention to Pd catalysts. Addition of Pd(OAc)$_2$ (10% molar ratio) to a THF solution of carbene complex **1a** and Et$_3$N, at room temperature, resulted within 1 h in a reaction mixture containing exclusively carbene dimer **2a** (2:1 *E/Z* mixture),[7] and a crystalline white solid identified as Cr(CO)$_6$.[8,9] Analogous results were obtained when the reaction was carried out at 0 °C, in other solvents (hexane, Cl$_2$CH$_2$, and Et$_2$O), or when lower catalyst loads (2% molar ratio) were used. The reaction of pentacarbonyl[(*p*-bromophenyl)(methoxy)carbene]chromium(0) (**1b**) gave similar results (Scheme 1). Complex **1b** also dimerized at room temperature in the presence of Pd(PPh$_3$)$_4$ (3% and 0.6% molar ratios) to yield olefin **2b**. The olefin *E/Z* ratios were identical to those obtained with Pd(OAc)$_2$/Et$_3$N, although a longer reaction time was needed when 0.6% of catalyst was employed. Even when carbene complex **1b** was reacted with Pd(OAc)$_2$ under the above conditions but in the presence of methyl acrylate, styrene, and 1-hexene, dimer **2b** was obtained exclusively and no traces of cyclopropane products were observed.[10]

Scheme 1



Scheme 2



The reactivity of Cr(0) carbenes **3a,b** was tested next. Both metal carbenes **3a,b** reacted at room temperature in the presence of 10% Pd(OAc)$_2$/Et$_3$N to give vinyl ethers **4a,b** and Cr(CO)$_6$, as the exclusive reaction products.[11] Dimers analogous to **2a,b** were not observed. Compound **4a** was unstable and could not be obtained analytically pure, while product **4b** could be isolated in 65% yield (Scheme 2). Clearly, the nature of the substituent at the carbene carbon set the nature of the reaction products. To determine the feasibility of intramolecular self-dimerization, we

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(1) For general reviews on the chemistry and synthetic applications of group 6 metal carbenes, see: (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissel, R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1983. (b) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587−608. (c) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, U.K., 1991; Vol. 5, pp 1065−1113. (d) Schwindt, M. A.; Miller, J. R.; Hegedus, L. S. *J. Organomet. Chem.* **1991**, *413*, 143−153. (e) Wulff, W. D. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 12, pp 470−547. (f) Hegedus, L. S. In ref 1e, pp 549−576. (g) Harvey, D. F.; Sigano, D. M. *Chem. Rev.* **1996**, *96*, 271−288. (h) Hegedus, L. S. *Tetrahedron* **1997**, *53*, 4105−4127. (i) Aumann, R.; Nienaber, H. *Adv. Organomet. Chem.* **1997**, *41*, 163−241.

(2) (a) Fischer, E. O.; Dötz, K. H. *Chem. Ber.* **1970**, *103*, 1273. (b) Dötz, K. H.; Fischer, E. O. *Chem. Ber.* **1972**, *105*, 1356−1367. (c) Fischer, E. O.; Dötz, K. H. *Chem. Ber.* **1972**, *105*, 3966−3973. Reviews: (a) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411−432. (b) Doyle, M. P. In ref 1e, pp 387−420. See also ref 1g.

(3) Unpublished results by K. H. Dötz cited in ref 1a, pp 196−197.

(4) Examples: (a) Takeda, K.; Okamoto, Y.; Nakajima, A.; Yoshii, E.; Koizumi, T. *Synlett* **1997**, 1181−1183. (b) Barluenga, J.; Aznar, F.; Fernández, M. *Chem. Eur. J.* **1997**, *3*, 1629−1637. (c) Barluenga, J.; Rodríguez, F.; Vadecard, J.; Bendix, M.; Fañanas, F. J. *J. Am. Chem. Soc.* **1996**, *118*, 6090−6091. (d) Takeda, K.; Takeda, M.; Nakajima, A.; Yoshii, E. *J. Am. Chem. Soc.* **1995**, *117*, 6400−6401. (e) Wang, S. L. B.; Su, J.; Wulff, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 10665−10666. (f) Fischer, H.; Schmid, J. *Chem. Commun.* **1985**, 572−573.

(5) See, for example: (a) Toledano, C. A.; Rudler, H.; Daran, J.-C.; Jeannin, Y. *Chem. Commun.* **1984**, 574−576. (b) Casey, C. P.; Vollendorf, N. W.; Haller, K. J. *J. Am. Chem. Soc.* **1984**, *106*, 3754−3764. (c) Söderberg, B.; Hegedus, L. S. *Organometallics* **1990**, *9*, 3113−3121. (e) Barluenga, J.; Monserrat, J. M.; Flórez, J. *Chem. Commun.* **1993**, 1068−1070.

(6) Sierra, M. A.; Casarrubios, L.; Domínguez, G. Unpublished results.

(7) The *E/Z* or product ratios were determined through this work by integration of well-resolved signals in the ^{1}H NMR spectra of the crude reaction mixtures prior to purification.

(8) The obtained white crystalline solid was identical (^{13}C NMR, IR, and EI mass spectra) to an authentic sample of Cr(CO)$_6$.

(9) All of the yields reported through this paper are for pure compounds, except for compound **4a**, which was unstable and could not be purified. See the Supporting Information for full experimental procedures and spectroscopic and analytical data. The following procedure for the self-dimerization of complex **1b** is representative: A THF solution (4 mL) of complex **1b** (312 mg, 1 mmol) was placed in a flame-dried airless flask containing a magnetic stirring bar and was degassed by evacuation/back-fill with argon (3×). Then, Pd(OAc)$_2$ (22 mg, 0.1 mmol) and Et$_3$N (0.15 mL, 1.1 mmol) were added at room temperature and the mixture was stirred for 1.5 h. The solvent was distilled under reduced pressure, and the residue was stirred in pentane and filtered through Celite. The solvent was removed in vacuo, and the residue (170 mg) containing an *E/Z* mixture (2:1) of olefin **2b** and Cr(CO)$_6$ was purified by molecular distillation to yield 120 mg (62%) of an *E/Z* mixture (2:1) of pure olefin **2b** as a colorless solid. The isomers [*E*-**2b**, 72 mg (37%); *Z*-**2b**, 32 mg (16%)] could be separated by flash chromatography (hexane/EtOAc, 10:1).

(10) Complex **1a** reacts with methyl acrylate in boiling cyclohexane to yield the corresponding cyclopropane. Wienand, A.; Reissig, H.-U. *Tetrahedron Lett.* **1988**, *29*, 2315−2318.

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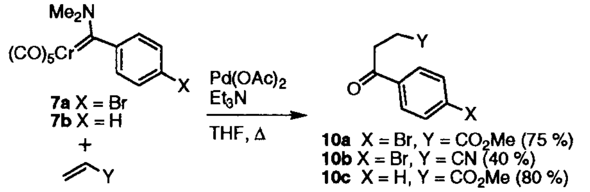
Scheme 3

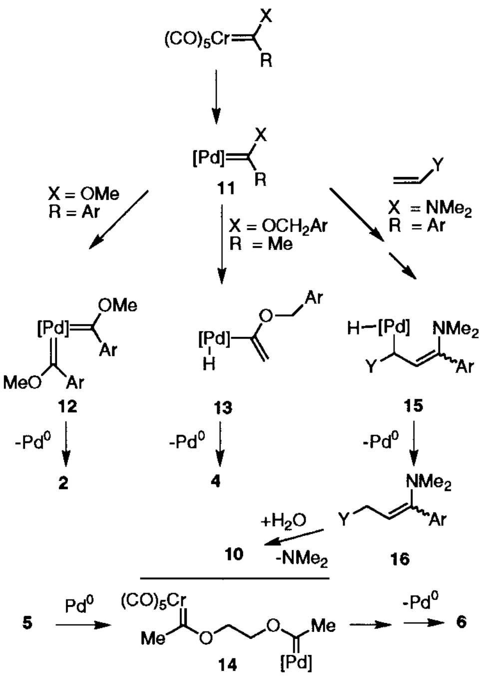


studied the reaction of bis-carbene complex **5**. By stirring a solution of complex **5** and Et$_3$N with Pd(OAc)$_2$ (10% molar ratio) at room temperature, cyclic carbene **6** was obtained (40% yield) after column chromatography (Scheme 2).[11] Compound **6** should arise from the intramolecular insertion of one carbene ligand into the acidic methyl group[12] bonded to the second carbene carbon.

Pentacarbonyl[(*N*,*N*-dimethylamino)(*p*-bromophenyl)carbene]-chromium(0) (**7a**) did not react at room temperature in the presence of Pd(OAc)$_2$ (10% molar ratio)/Et$_3$N. Increasing the temperature resulted in the formation of *N*,*N*-dimethyl-*p*-bromobenzamide (**8**) and *p*-bromobenzaldehyde (**9**) after prolonged reaction times.[13] Complex **7a** was then reacted with methyl acrylate and acrylonitrile in the presence of Pd(OAc)$_2$ (10% and 2% molar ratio)/Et$_3$N in boiling THF. γ-Ketoester **10a** (75%) and γ-ketonitrile **10b** (40%) were obtained, respectively.[9] Small amounts of amide **8** and aldehyde **9** were obtained in both cases. Reaction of complex **7b** with methyl acrylate and Pd(OAc)$_2$ (2%)/Et$_3$N gave γ-ketoester **10c** (80%) (Scheme 3).[14] The reaction of complex **7a** with methyl acrylate, using Pd(PPh$_3$)$_4$ (10% molar ratio) as the catalyst gave results analogous to those obtained in the reaction with Pd(OAc)$_2$.[15]

The observed reactivity of the Cr(0)−carbene complexes may be explained by the initial formation of intermediate Pd carbenes **11**.[16] Thus, for aryl-substituted alkoxycarbenes, double transmetalation would form bis-carbene **12**, which evolves to olefins **2** by elimination of Pd^0 regenerating the catalyst.[17] The presence of a β-hydrogen in complex **11** would allow its transfer to the metal center to occur, leading to **13** apparently faster than transfer of a second carbene moiety from a Cr complex would produce the bis-carbene **12**. With the dicarbene complex **5**, transmetalation of one of the carbene moieties to Pd leads to a heterobimetallic intermediate **14**. Insertion of the Pd center in a methyl C−H bond of the remaining Cr−carbene moiety followed by β-hydrogen elimination would lead to the observed carbene product **6**.

Scheme 4



For aminocarbenes the transmetalation to Pd seems to be productive only when a carbene acceptor is present. The observed products **16** would result from cyclization of the Pd carbene and carbene acceptor followed by transfer of a β-H to the metal center (**15**) and reductive elimination.[18] Hydrolysis of **16** during workup would account for the obtained β-keto derivatives **10** (Scheme 4).

In conclusion, unprecedented new catalytic processes of alkoxy- and aminochromium carbene complexes have been observed. Reactions leading to self-dimerization, β-elimination, and alkyl and vinyl C−H insertion can be carried out with the above complexes in the presence of Pd(AcO)$_2$ at room temperature or below (for alkoxy-substituted complexes) or with shorter reaction times than the uncatalyzed processes with amino-substituted complexes. Efforts to obtain other reaction products by employing modified catalysts and to develop new catalytic processes to prepare novel Cr(0) carbenes are now under way in our laboratories.

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Supporting Information Available: Text describing the full experimental procedure for the preparation of compounds **1b**, **2a,b**, **3b**, **4b**, **6**, **7a,b**, and **10a**−**c**, including characterization data, and copies of ^{1}H and ^{13}C NMR spectra of compound **4a** (8 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(11) Complexes **3b** and **5** were recovered unaltered after stirring with Et$_3$N in THF, and in the absence of catalyst, at room temperature for 3 h.

(12) The hydrogens attached to the carbene α-carbon of group 6 metal carbenes are acid: (a) Casey, C. P.; Anderson, R. L. *J. Am. Chem. Soc.* **1974**, *96*, 1230−1231. (b) Gandler, J. R.; Bernasconi, C. F. *Organometallics* **1989**, *8*, 2282−2284. (c) Bernasconi, C. F.; Sun, W. T. *J. Am. Chem. Soc.* **1993**, *115*, 12526−12532. (d) Bernasconi, C. F.; Sun, W. T. *Organometallics* **1997**, *16*, 1926−1932. (e) Bernasconi, C. F.; Leyes, A. E. *J. Am. Chem. Soc.* **1997**, *119*, 5169−5175. (f) Bernasconi, C. F.; Sun, W.; Garcia-Rio, L.; Yan, K.; Kittredge, K. *J. Am. Chem. Soc.* **1997**, *119*, 5583−5590.

(13) Cleavage of the metal−carbene bond on alkoxychromium(0) carbenes to form aldehydes takes place in the presence of different reagents. (a) HBr, Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 6726−6727. (b) Urotropin/H$_2$O, Aumann, R.; Hinterding, P.; Krüger, C.; Goddard, R. *J. Organomet. Chem.* **1993**, *459*, 145−149.

(14) Products derived from the Heck's coupling on the aryl bromide were not observed, although it has been described that organic substrates related to complexes **7** produced high yields of coupling products under analogous reaction conditions to those employed by us. See: Heck, R. F. *Org. React.* **1982**, *27*, 345−390. The Stille's coupling of pentacarbonyl[[(tributylstannyl)-ethinyl](dimethylamino)carbene]chromium(0) and tungsten(0) complexes and diverse organometallic iodides, in the presence of PdCl$_2$(MeCN)$_2$ in toluene at room temperature, has been reported recently: Hartbaum, C.; Roth, G.; Fischer, H. *Chem. Ber.* **1997**, *130*, 479−488.

(15) Compounds analogous to **10a**−**c** are formed by heating pentacarbonyl-[(*N*,*N*-dimethylamino)methylene]chromium(0) and some olefins. See: Sierra, M. A.; Soderberg, B.; Lander, P. A.; Hegedus, L. S. *Organometallics* **1993**, *12*, 3769−3771. To discard that compounds **10a**−**c** were formed without the participation of the Pd catalyst, complex **7a** was reacted with methyl acrylate in boiling THF and in the absence of catalyst. A mixture of *N*,*N*-dimethyl-*p*-bromobenzamide (**8**) and γ-ketoester (**10a**) (4:1 ratio) was obtained after 48 h. The different product ratio and the shorter reaction times (8 h) for the catalytic reaction point to the participation of Pd intermediates in the reactions of complexes **7a,b**.

(16) For reviews on the preparation and reactivity of Pd−carbene complexes, see: (a) Maitlis, P. M.; Espinet, P.; Russell, M. J. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 6, pp 292−299. (b) Dixon, K. R.; Dixon, A. C. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 9, pp 216−219. The stoichiometric transfer of carbene ligands from group 6 mononuclear metal−carbene complexes to group 10 metal centers has been reported: Ashworth, T. V.; Berry, M.; Howard, J. A. K.; Laguna, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1615−1624.

(17) Oxidative coupling of an acyl ligand with a carbene ligand on a Cr center promoted by iodine to form α-alkoxy enones has been reported. Wieber, G. M.; Hegedus, L. S.; Gale, C. *Organometallics* **1995**, *14*, 3574−3577.

(18) An alternative reaction pathway may involve transmetalation to Pd from the chromacyclobutane formed by cyclization of the Cr carbene and the carbene acceptor. This fact may account for the observed inertia of aminochromium(0) carbenes in the absence of a carbene acceptor. The overall outcome of the reaction would be identical in this case.