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Novel Alkylation−Annulation Reaction of Fischer Carbene Complexes[†]

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Summary: Alkylation of aminocarbene complexes $(CO)_5M{=}C(CH_3)(NHR)$ *with dichloromethane or dibromomethane under PTC conditions triggers an annulation reaction leading to novel cyclic products. This is the first example of such reactivity of Fischer carbene complexes.*

Fischer carbene complexes are often compared with esters or amides in terms of reactivity patterns,[1] viz. stabilization of α-carbanion and consequent alkylation[2] or aldol reactions,[3] and participation of conjugated multiple bonds in Michael addition[4] or Diels−Alder reaction.[5] It has been recognized that the $C{=}M(CO)_5$ fragment is far more electrophilic than a C=O function, and that is reflected in the pK_a of the α-proton[6] as well as in the relative rate of Diels−Alder reactions.[5] Also, displacement of the alkoxy group of a Fischer carbene complex by a different alcoholate or an amine,[7] which presumably proceeds *via* a tetrahedral intermediate, is reminiscent of ester exchange or ester aminolysis, respectively. Reaction of a carbon nucleophile at the carbene carbon leading to the displacement of the alkoxide group[8] parallels the synthesis of ketones from esters. In this report, we wish to describe the first example of an intramolecular aldol−dehydrometalation reaction involving the metal−carbene fragment of amino Fischer carbene complexes, in which the C=M bond behaves more like the C=O function of a ketone rather than that of an ester or an amide.

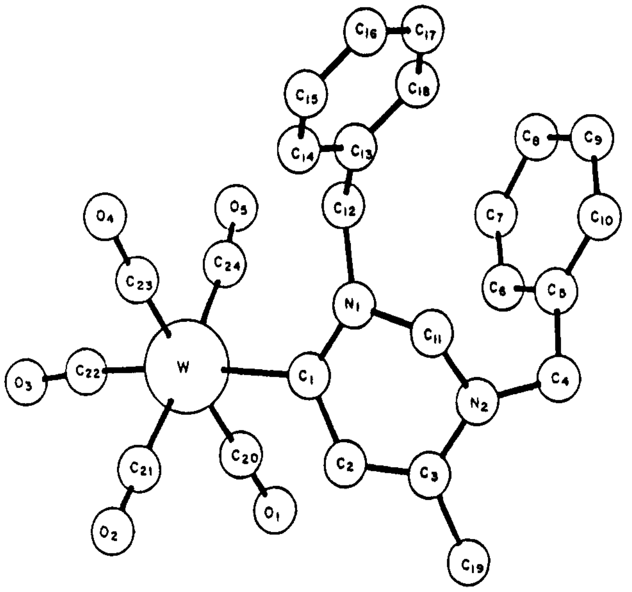

Figure 1. Crystal structure of **2a**. Important bond distances (Å) and angles (deg): W−C(1), 2.30(2); C(1)−C(2), 1.40(3); C(2)−C(3), 1.38(3); C(3)−N(2), 1.35; W−C(1)−N(1), 127.2(12); W−C(1)−C(2), 117.3(13); C(1)−N(1)−C(11), 114.3(14); C(1)−C(2)−C(3), 119.8(17); N(1)−C(11)−N(2), 110.2(14); C(2)−C(3)−N(2), 117.1(17); C(3)−N(2)−C(11), 111.2(16); N(1)−C(1)−C(2), 115.2(16).

When a solution of the aminocarbene complex **1a** in dichloromethane was stirred with 50% aqueous NaOH and a catalytic amount of Bu_4NBr for 4 h at room temperature,[2a,9] a new product was formed, which was isolated by flash chromatography. Presence of a $(CO)_5W{=}C$ fragment in this compound was confirmed

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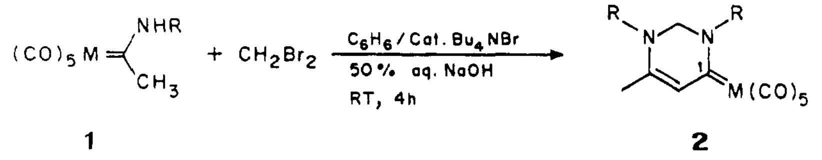
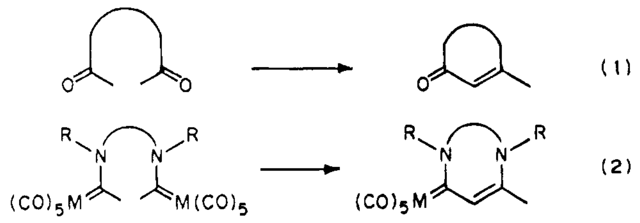
Scheme 1[a]



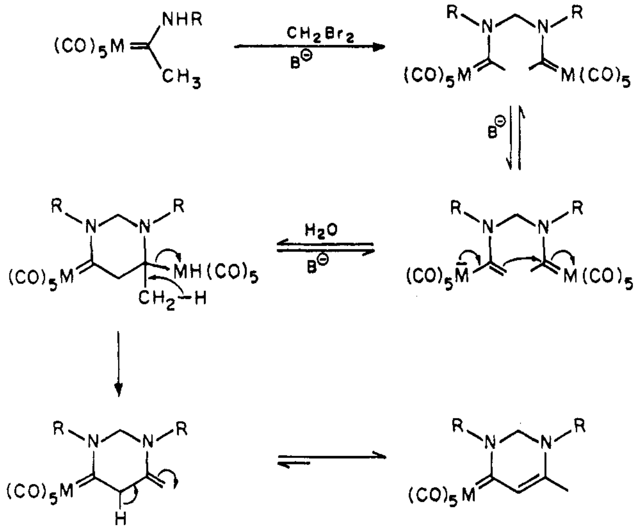
	M	R		M	R	Yield[a] (%)	^{13}C (C-1) δ (PPM)
a	W	CH_2Ph	a	W	CH_2Ph	73	215·9
b	W	$CH_2CH{=}CH_2$	b	W	$CH_2CH{=}CH_2$	71	215·6
c	W	CH_3	c	W	CH_3	80	217·3
d	Cr	CH_2Ph	d	Cr	CH_2Ph	76	232·3
e	Cr	CH_3	e	Cr	CH_3	87	233·0

[a] Isolated yield based on recovered starting material (5–10%).

Scheme 2



Scheme 3



by IR spectroscopy. The structure of this new complex was conclusively determined by X-ray crystallography (Figure 1).

The complex **2a** was found to be a cyclic compound with an unusually electron-rich metal–carbene moiety. Clearly, this product resulted from the reaction of two molecules of the starting complex linked by a methylene group derived from dichloromethane. The ^{1}H NMR spectrum was readily interpreted on the basis of this structure. The singlet at 2.25 ppm was assigned to the vinylic methyl group. Of the two sets of benzylic methylene protons, one appeared together with the $N{-}CH_2{-}N$ protons as a singlet at 4.25 ppm and the other appeared as a singlet at 5.10 ppm. The olefinic proton appeared as a singlet at 6.60 ppm. The most deshielded ^{13}C NMR signal at 215.9 ppm was assigned to the carbene carbon, while the CO resonances appeared at 203.8 and 199.7 ppm. The carbene carbon is shielded by about 46 ppm compared to the amino carbene complex **1a**, the most shielded carbene carbon observed so far.[10]

A series of aminocarbene complexes **1b–e** undergoes a similar reaction with good to excellent yields (Scheme 1). It was found that replacement of dichloromethane (solvent) by an equivalent amount of dibromomethane in benzene significantly improved the yields.[11] Formation of the cyclic product **2e** from **1e** was also effected by the use of BuLi instead of NaOH at −78 °C.

This novel annulation reaction has a close parallel in Robinson annulation[12] of carbocyclic systems, as represented in Scheme 2. In an annulation reaction (eq 1 of Scheme 2), a diketone can cyclize by an intramolecular aldol condensation followed by dehydration. In the present example, a possible intermediate bearing two $(CO)_5M{=}C(CH_3)(NRR')$ functionalities undergoes a similar cyclization under mild conditions (eq 2). This is a unique reaction of Fischer carbene complexes. First, it implies facile formation of a carbanion adjacent to an aminocarbene function and its reaction with a $C{=}M(CO)_5$ group intramolecularly. Secondly, a dehydrometalation is observed in preference to the expulsion of the amino group (as is common in acylation reactions). Such a reaction is characteristic of ketones or aldehydes in an aldol reaction and certainly not observed with esters or amides. Thus, the present reaction provides the first example of intramolecular *metalla–aldol*[13] reaction of Fischer carbene complexes.

A possible mechanism of this reaction is depicted in Scheme 3. Since (dialkylamino)carbene complexes did not undergo such a reaction, it is most probable that

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[10] For a recent report on acyclic Fischer carbene complexes containing similar functional groups but prepared by an entirely different route, see: Stein, F.; Duetsch, M.; Pohl, E.; Herbst-Irmer, R.; de Meijere, A. *Organometallics* **1993**, *12*, 2556. The most shielded of the carbene carbons described therein appears at 258.75 ppm.

[11] Typical procedure: The carbene complex (*n* mmol) and tetrabutylammonium bromide (0.1*n* mmol) in benzene was treated with 50% aqueous NaOH and dibromomethane (*n* mmol). The mixture was stirred at room temperature under argon for 4 h. The reaction mixture was diluted with water, extracted with dichloromethane, dried, and concentrated under reduced pressure. The pure product was isolated by flash chromatography using dichloromethane (5–50%) in petroleum ether as the eluant.

[12] (a) Gawley, R. E. *Synthesis* **1976**, 777. (b) Jung, M. E. *Tetrahedron* **1976**, *32*, 3.

[13] We prefer the term "metalla–aldol", suggested by Prof. T. R. Hoye, to distinguish this reaction from closely related ones (see: Casey, C. P.; Brunsvold, W. R. *Inorg. Chem.* **1977**, *16*, 391). Here the C=M group not only acts as the electrophile for carbanion addition in an aldol fashion, it is also sacrificed in the subsequent dehydrometalation step (akin to dehydration), which is a unique feature of this reaction.

N-alkylation by dihalomethane precedes cyclization. Thus, the first step is N-alkylation of the aminocarbene complex by dichloromethane to produce a bis-carbene complex. This was confirmed by the use of CD_2Cl_2 as solvent, which resulted in the disappearance of the methylene singlet at 4.30 ppm in the ^1H NMR spectrum of the product **2e** (Scheme 1). This complex can undergo an intramolecular aldol-type reaction in which a C=M bond is attacked by a proximate carbanion. β-Elimination followed by double-bond isomerization leads to the product.[14]

The feasibility of carbanion formation (pK_a of aminocarbene complexes is estimated[4a] to be about 20) under these conditions was substantiated by D_2O exchange (CH_2Cl_2/50% NaOD in D_2O with catalytic amount of Bu_4NBr) of methyl(benzylmethylamino)carbene tungsten complex. In 4.5 h, about 75% deuterium incorporation was observed.[15] Although C-alkylation of this complex could not be effected under similar conditions, intramolecular condensation reported herein probably occurs owing to favorable entropy.

Indeed, such a reaction is not common in amide chemistry, and this result shows that Fischer carbene complexes can display a wider range of reactivity than one anticipates merely in terms of analogy and precedents. The novel cyclization product has interesting structural features. In a way, the amino carbene complex **2** is also an enamine and thus constitutes an unusual push–pull system. The reactive sites of these complexes are located at the C=M bond as well as the enamine function. The chemistry of this new class of complexes as well as their heteroatom analogs is currently being explored.

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Supporting Information Available: Spectral data (^1H and ^{13}C NMR) of all compounds and tables giving details of X-ray analysis, atomic coordinates, thermal parameters, and bond lengths and bond angles of **2a** (20 pages). Ordering information is given on any current masthead page.

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[14] Alternatively, one of the methylene protons might be lost in the dehydrometalation step, as suggested by one of the referees.

[15] There is also a noticeable change in the conformer ratio as observed in the ^1H NMR spectrum, which is an indirect evidence for the deprotonation of the methyl group. An α-carbanion competes with delocalization of the lone pair of nitrogen toward the C=M bond. This reduces the rotation barrier of $C_{carbene}$–N bond and facilitates conformational interchange.