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Preliminary communication

ACTIVATION OF ALKYLIDENE-BRIDGED HETEROBIMETALLIC COMPLEXES TOWARD ELECTROPHILIC ATTACK

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Summary

Treatment of alkylidene-bridged zirconium-aluminum species with HMPA renders the C—Al bond of the alkylidene unit susceptible to electrophilic attack; in the absence of HMPA, the C—Zr bond is attacked.

Tebbe's compound [1] (Ia) is now established [2] as a useful methylenation reagent for carbonyl groups of aldehydes, ketones and esters; as such it broadens in scope "Wittig"-type olefination procedures for organic synthesis. To create general alkylidene transfer reagents, we had prepared [3] long-chain alkylidene-bridged bimetallic complex analogs of the "Tebbe" reagent. Titanium-based complexes (I) do react as "Wittig"-type reagent species but could be prepared, however, only in low yield. In contrast, zirconium-based analogs (II), which can be prepared easily and in high yield, are not active Wittig reagents, but react instead with carbonyl-containing compounds by hydride transfer to give reduced products. This difference in reactivity between Ti- and Zr-based analogs (I and II) appears to be a general phenomenon: Negishi [4] has synthesized a series of Zr- and Ti-alkenylidene-bridged aluminum species and has reported that although vinylidene-bridged titanium complexes convert cyclohexanone or benzaldehyde into allenes, the corresponding zirconium analogs do not behave in the same fashion. Clearly, to capitalize on the ease of synthesis of zirconium-based alkylidene-bridged species and to develop them as alkylidene transfer reagents requires an understanding of factors which underlie differences between them and their titanium-based analogs. For example, electronegativity differences between titanium and zirconium could control the site of electrophilic attack upon these two different types of metallic species. In fact, we have now demonstrated that I and II exhibit different reactivity patterns with regard to attack by simple electrophiles. These results may, in turn, bear on the question of relative reactivities of I and II with more complex species such as carbonyl group-containing organics.

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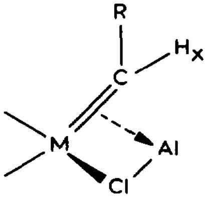
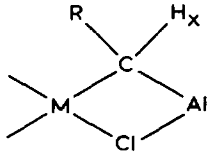
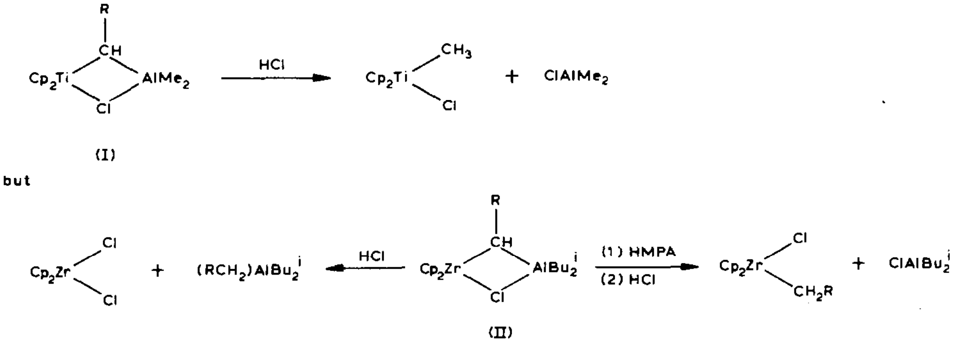
Two extremes for representation of bonding in I or II can be envisaged: aluminum-stabilized carbene complex A and bimetallic alkylidene (alkyl-like) species B. Compounds best represented by A should exhibit a different point of susceptibility toward electrophilic attack than should those best described by B. In fact, when a solution of Ia (0.05 *M* in toluene) is treated with 1 equiv. of HCl (at −40°C) specific cleavage of the C—Al bond occurs to give $Cp_2Ti(Me)Cl$ and $ClAlMe_2$. This is consistent with a description of such Ti/Al complexes I as nucleophilic titanium(II) carbenoids (Form A). In contrast we find that treatment of a solution of IIa (0.18 *M* in toluene) with 1 equiv. HCl (−40°C) results in selective cleavage of the Zr—C bond. The Zr complex does not react readily, therefore, as a nucleophilic zirconium(II) carbene, and it may be better represented by form B (in other words, II may be more zirconium(IV) alkylidene-like). This notion of greater "carbene"-like character for the Ti complex compared with its Zr analog is further substantiated by noting different ^1H NMR chemical shifts for H_X: for Ia, δ 8.49 ppm; for IIa, δ 7.02 ppm.



(A)



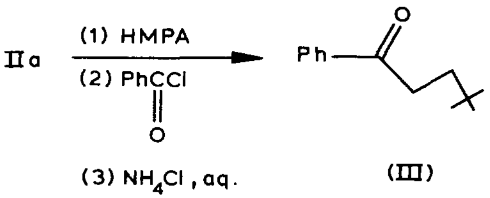
Coordination of a donor ligand to the Al in IIa should build up negative charge on it thus labilising the C—Al bond and making IIa more "carbenoid" (Form A) in character. Low temperature ^1H and ^{31}P NMR analysis shows that HMPA forms a complex with IIa (on mixing at −30°C) by ligation at Al, and, in fact, adding 1 equiv. HMPA to a solution of IIa (0.20 *M* in toluene, −40°C) followed by addition of one equivalent of HCl results in specific cleavage of the C—Al bond, to give $Cp_2Zr(R)Cl$ and $ClAl(i\text{-}Bu)_2(HMPA)$, analogous with that noted for pure, uncomplexed I and consistent with a relative electronegativity ordering Ti > Al > Zr > Al(HMPA).



(Ia, R = H; IIa, R = neopentyl)

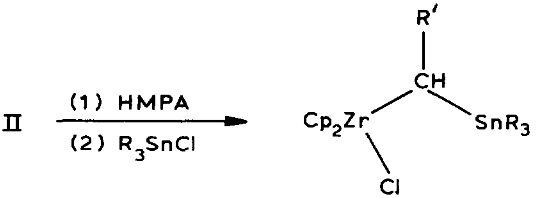
SCHEME 1

Tebbe's reagent has been reported to react with acyl halides in the presence of pyridine to yield titanocene enolates [5]. In parallel with our observations concerning reactivity with HCl, IIa does not react with benzoyl chloride, either in the absence or presence of pyridine, to yield the analogous enolate. However, treating IIa (0.125 *M* in toluene) successively with 1 equiv. HMPA (−40°C) and 1 equiv. benzoyl chloride gives III on hydrolysis in a yield comparable (24%) to that reported for Ia. Clearly, then, a stronger aluminum-ligating species [6] is necessary to activate Zr-based reagents than is required for I [7].



SCHEME 2

Ligand-based activation of the C—Al bond can also be used to convert II to other bimetallic species. Thus treatment of II with HMPA followed by addition of a weakly electrophilic metal salt can give rise to a new heterobimetallic species. For example, by slowly adding a toluene solution of R_3SnCl (0.25 *M*) to a toluene soln of II (0.25 *M*) and 1 equiv. HMPA at −40°C, followed by warming to room temperature and then by stirring for 4 h, IV can be produced in ca. 60—100% yield (depending on R and R′). Complex IVa can be isolated by concentrating the toluene solution, adding pentane, removing the yellow supernatant from the precipitate formed, and passing it through a plug of basic alumina under N_2. Recrystallization from pentane gives bright yellow crystals of IVa [8]. Attempts to purify IVb by the same method did not remove traces of Ph_3SnCl. Treating IV with either Ph_3SnCl or Me_3SnCl in the absence of HMPA gave only Cp_2ZrCl_2 and unidentified organic decomposition products [9].



(IV)

IVa : R = CH_3 , R′ = $(CH_2)C(CH_3)_3$ (75 %^{a}, quantitative by NMR)

IVb : R = Ph , R′ = $(CH_2)C(CH_3)_3$ (82 %)^b

IVc : R = CH_3 , R′ = $(CH_2)_4CH_3$ (58 %)^b

SCHEME 3. ^{a}Isolated yield. ^{b}By NMR.

Success of an alkylidene-bridged heterobimetallic complex such as I or II as a "Wittig" reagent depends on the relative ability of a given species to attack a coordinated carbonyl group as a carbon "nucleophile" or, if present, to transfer a β-hydride to it. We are now preparing a series of alkylidene-bridged zirconium-heteroatomic species capable of showing high carbon bond nucleophilicity.

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7 Complex IIa treated with HMPA showed enhanced Wittig activity toward cyclohexanone relative to that of unactivated IIa but, however, not at a synthetically useful level; this may derive from displacement of HMPA from Al by the carbonyl group of the ketone.
8 For IVa: ^{1}H NMR (C_6D_6): δ 5.87 (s, 5H), 5.84 (s, 5H), 1.92—2.36 (AB_2 pattern, 3H, *J* 12.8 Hz), 0.94 (s, 9H), 0.13 ppm (s with Sn satellites, 9H, *J*(Sn-H) 43.4, 46.8 Hz); ^{13}C NMR: δ 112.67, 111.48, 59.69, 48.15, 34.17, 29.67, −5.05 ppm; Anal.: Found: C, 45.04; H, 6.02; Cl, 6.96; Sn, 23.75. $C_{19}H_{31}ClSnZr$ calcd.: C, 45.21; H, 6.19; Cl, 7.02; Sn, 23.51; Zr, 18.07%. *m/e* = 504; (quantitative yield by NMR; 75% yield of recrystallized material). For IVb: ^{1}H NMR: δ 7.7—7.5 (m, 6H), 7.10—7.25 (m), 5.89 (s, 5H), 5.79 (s, 5H), 2.0—2.6 (m-3H), 0.90 ppm (s, 9H); (82% by NMR).
For IVc: ^{1}H NMR: δ 5.89 (s, 5H), 5.86 (s, 5H), 0.17 ppm (s with Sn satellites, 9H); (58% by NMR).
9 Treating IIa with Cp_2TiCl_2 in similar fashion in the presence of HMPA gave a species tentatively identified as $Cp_2Ti(Cl)(CH[neopentyl])Zr(Cl)Cp_2$ (V); ^{1}H NMR: δ 6.049 (s, 5H), 6.044 (s, 5H), 5.970 (s, 5H), 5.965 (s, 5H), 0.943 ppm (s, 9H).