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Preliminary communication

STABLE ACYLS AND IMINOACYLS OF ZIRCONIUM(IV), $[Zr(\eta\text{-}C_5H_5)_2\{C(:X)R\}R']$ [X = O OR NTol-*p*; R = Me_3CCH_2, Me_3SiCH_2, OR $(Me_3Si)_2CH$; R′ = Cl OR ALKYL]

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Summary

Insertion of CO or *p*-TolNC into a Zr—C bond of $[Zr(\eta\text{-}C_5H_5)_2(R)R']$ under ambient conditions in C_6H_6 leads to the stable η^2-acyl- or η^2-iminoacyl-complex $[Zr(\eta\text{-}C_5H_5)_2\{\eta^2\text{-}C(X)R\}R']$ (X = O or NTol-*p*); with $[Zr(\eta\text{-}C_5H_5)_2\{CH(SiMe_3)_2\}Me]$ as substrate there is exclusive preference for scission of the more hindered Zr—C bond.

We report the preparation and spectroscopic characterisation of some new acyls and iminoacyls of Zr^{IV} (I), obtained by the insertion reaction of eq. 1 under ambient conditions in benzene.

$$\underset{\text{(II)}}{[Zr(\eta\text{-}C_5H_5)_2(R)R']} + CX \xrightarrow{X\,=\,O\text{ or NTol-}p} \underset{\text{(I)}}{[Zr(\eta\text{-}C_5H_5)_2\{C(:X)R\}R']} \qquad (1)$$

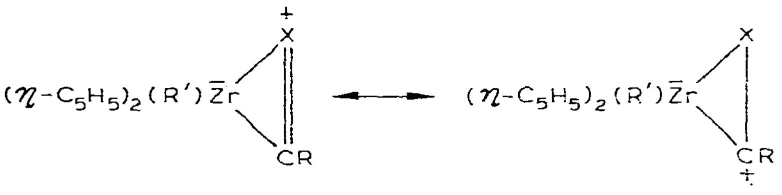
TABLE 1

SELECTED DATA FOR THE NEW ACYL AND IMINOACYL COMPOUNDS $[Zr(\eta\text{-}C_5H_5)_2\{\eta^2\text{-}C(X)R\}R']$[a]

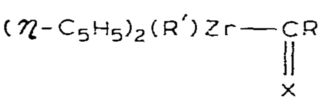
X	R	R′	ν(C=X) (cm^{-1})[b]	^{13}C NMR: δ(C=X)[c] (ppm)
O	CH_2CMe_3	Cl	1550	318.7
O	CH_2SiMe_3	Cl	1515	317.2
O	CH_2CMe_3	CH_2CMe_3	1560	322.9
O	CH_2SiMe_3	CH_2SiMe_3	1505	
O[d]	$CH(SiMe_3)_2$	Me	1470	
NTol-*p*	$CH(SiMe_3)_2$	Cl	1540, 1520	238, 233.2
NTol-*p*[e]	$CH(SiMe_3)_2$	Me	1530	241.6, 237.9
NTol-*p*	CH_2SiMe_3	CH_2SiMe_3	1578	242.4
NTol-*p*	CH_2CMe_3	CH_2CMe_3	1578	245.8

[a] These are white-to-pale yellow, crystalline compounds having sharp m.p.'s and analysing satisfactorily; only representative compounds and spectroscopic data are cited. [b] Nujol mull. [c] In $CDCl_3$ solution. [d] ^1H NMR: 5.63 (η-C_5H_5), 3.78 ($\overset{O}{\overset{\|}{C}}$-CH), 0.57 (Zr-$CH_3$), 0.20 ($SiMe_3$). [e] ^1H NMR: 6.5-7.3 (C_6H_4), 5.77 (η-C_5H_5), 2.95 [CHC(:NTol-*p*)], 2.45 (CH_3Tol-*p*), 0.23 ($SiMe_3$), −0.07 (Zr-CH_3).

The results are summarised in Table 1. The following features are of interest. (i) Several simple neutral iminoacyls of Zr^{IV} are reported.* (ii) The use of an unsymmetrical dialkylzirconium(IV) substrate, (II) [R = $(Me_3Si)_2CH$, R′ = Me], provides for the first time an opportunity to examine competitive insertion, and exclusive preference with both CO or *p*-TolNC is for scission of the more hindered (also the weaker [1]) Zr—C bond in I. (iii) The title acyls I (X = O) are stable crystalline solids which do not dissociate into their factors (reverse of eq. 1) in solution at 25°C, in contrast to their labile methyl or benzyl analogues I (R = Me or $PhCH_2$, X = O) [2]. (iv) Spectroscopic data point to an η^2-, (III), rather than η^1-, (IV), mode of attachment of the acyl or iminoacyl ligand, as has previously been unequivocally demonstrated (including X-ray) for $[Zr(\eta\text{-}C_5H_5)_2(COMe)Me]$ [2]. As for (iv), the low ν(CX) IR absorption for compounds I (see Table 1) provides good evidence for structure (III) for the acyl complexes, cf., 1540 cm^{-1} when X = O and R = Me = R′ [2]. However, it is less clear cut for the nitrogen analogues, cf., 1680-1700 cm^{-1} in $[Mo(\eta\text{-}C_5H_5)_2\{\eta^2\text{-}C(NPh)Me\}CO]$ [3]. The low ^{13}C NMR chemical shifts for both types, however, support the sideways-on ligating mode, cf., $\delta(^{13}C)$ for the above Mo^{II} complex at ca. 195 ppm downfield from $SiMe_4$ [3].

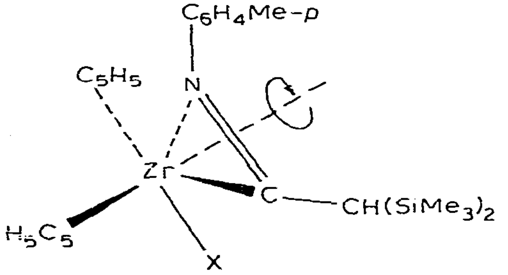


(III)



(IV)

One of the iminoacyl complexes I (X = NTol-*p*, R = $(Me_3Si)_2CH$, and R′ = Cl) shows NMR characteristics at ambient temperature indicative of two isomers and also has two ν(NC) IR bands. Thus in the ^{13}C NMR experiment at 25°C each carbon signal is a 1/1 doublet in $CDCl_3$, but a 3/1 doublet in C_6D_6 in which solvent coalescence occurs at 65°C. We attribute this to the rota-



(V) (X = Cl)

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*Compounds containing the group $Zr^{IV}\{C(:NR)C(Ph):CMe_2\}$ have been obtained by RNC insertion into a Zr^{IV}—alkenyl bond [5].

tion described in V, which is sufficiently slow to be observed on the NMR time scale only when R is the bulky $(Me_3Si)_2CH$ group. This spectroscopic observation cannot be explained in terms of η^1-attachment of the iminoacyl ligand [3].

A rapid reaction is also observed when either CO or *p*-TolNC is allowed to react with the dimeric hydridoalkyl II ($R = (Me_3Si)_2CH$, $R' = H$) [1] under ambient conditions; it is likely that competitive pathways are operative [4]. Experiments are in progress to resolve this issue, as well as on (i) an X-ray diffraction study of an iminoacyl (I) and (ii) variable temperature ^{13}C NMR.

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