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Preliminary communication

HOMOLEPTIC ALKENYLS OF THE EARLY TRANSITION METALS AND RELATED COMPOUNDS

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Summary

The first stable homoleptic alkenyls of the early transition metals, MR_n, ($R = C(Ph)=CMe_2$; M = Ti, Zr, Hf, $n = 4$, and M = Cr, $n = 3$) and the related species $(C_5H_5)_2MR_2$ (M = Ti, Zr) and $(C_5H_5)_2Zr(Cl)R$ have been prepared using appropriate organolithium reagents Cleavage and insertion reactions are reported for the new compounds.

There has been much interest in homoleptic alkyls of the early transition metals [1,2], and in their catalytic roles [3]. Relatively little is known about σ-bonded, α-unsaturated hydrocarbonics [4], and stable homoleptic derivatives of the early transition metals have so far not been described for these ligands (see e.g. ref. 5)

Such alkenyls are, however, of interest in several ways (i) synthesis of stable species and comparison with related saturated molecules, (ii) the relevance of the β-elimination pathway as a mode of decomposition, (iii) structure. including possible multiple bonding between metal and $C(sp^2)$, for some compounds, and (iv) reactivity, including catalytic activity. We now report the synthesis and some reactions of the first stable, σ-bonded homoleptic alkenyls of Ti, Zr, Hf, and Cr.

Although we recognise that alkenyls by virtue of their geometry and unsaturation may be inherently more stable than alkyls to the β-elimination reaction, we sought initially to prepare compounds in which this pathway was blocked by appropriate substitution, and in which the ligands had bulky substituents α to the metal atoms. Of the ligands so far studied, 2,2-dimethyl-1-phenylvinyl has proved particularly successful, and we have prepared and characterised by satisfactory elemental analysis, NMR data, or both, the species TiR_4, ZrR_4 HfR_4, CrR_3, $(C_5H_5)_2TiR_2$, $(C_5H_5)_2ZrR_2$, and $(C_5H_5)_2Zr(Cl)R$ where $R = C(Ph)=CMe_2$. Physical properties and spectroscopic data are presented in Table 1.

TABLE 1

ALKENYLS OF THE EARLY TRANSITION METALS

Compound[a]	Colour	M p (°C)	$\delta(CMe_2)$[b]	$\delta(Ph)$[b]	Other data
TiR_4	Yellow	-	1 24 s(3) 1 95 s(3)	7 22 m(5)	Impure, dec > —20°C
ZrR_4	Off-white	70 (dec)	1 35 s(3) 1 89 s(3)	7 18 m(5)	Stoichiometry also by NMR titration, crystalline
HfR_4	Off-white	70 (dec)	1 33 s(3) 1 87 s(3)	7 11 m(5)	Crystalline
CrR_3	Dark green	116—118 (dec)	1 40 s(3) 1 73 s(3)	7 20 m(5)	Crystalline
$(C_5H_5)_2TiR_2$	Light red	120 (dec)	1 39 s(3) 1 91 s(3)	7 17 m(5)	δ(Cp), 5 66 s(5), crystalline
$(C_5H_5)_2ZrR_2$	Yellow	174 (dec)	1 50 s(3) 1 88 s(3)	7 20 m(5)	δ(Cp), 5 94 s(5), crystalline
$(C_5H_5)_2Zr(Cl)R$	Pale yellow	170 (dec)	1 44 s(3) 1 65 s(3)	7 15 m(5)	δ(Cp) 6 25 m(10), crystalline

[a] R = 2,2-dimethyl-1-phenylvinyl

[b] Chemical shift (ppm) relative to internal TMS, in benzene s = singlet, m = multiplet, relative intensities in brackets For Ph resonance the most intense peak is noted

The compounds, which are air- and moisture-sensitive solids, can however be handled at room temperature both in the solid phase or in solution under pure dry nitrogen or argon The homoleptic titanium species is apparently better handled at —20°C or below, at least until thoroughly pure, to avoid slow decomposition.

The alkenyl ligands are rapidly cleaved by protic species (see Scheme 1) giving alkene Rupture of the metal—carbon bond also appears to be the initial photochemical process for the compounds $(C_5H_5)_2ZrR_2$ and $(C_5H_5)_2Zr(Cl)R$ in $CDCl_3$ Irradiation with light of wavelength greater than 390 nm yields $(C_5H_5)_2Zr(Cl)R$ and $(C_5H_5)_2ZrCl_2$ respectively

Insertion reactions, particularly with methyl isonitrile, proceed cleanly and essentially quantitatively at room temperature. With ZrR_4, the tetra-insertion product (A), was obtained, and this behaviour contrasts with that of $(C_5H_5)_2ZrR_2$ (Scheme 1) Under similar conditions the alkenyls are apparently not 1,2-dipolarophiles, failing to react with phenyl isocyanate, phenyl isothiocyanate, and dimethyl acetylenedicarboxylate

Related compounds of tin have been prepared for structural and photochemical comparison, and details will be reported elsewhere [6].

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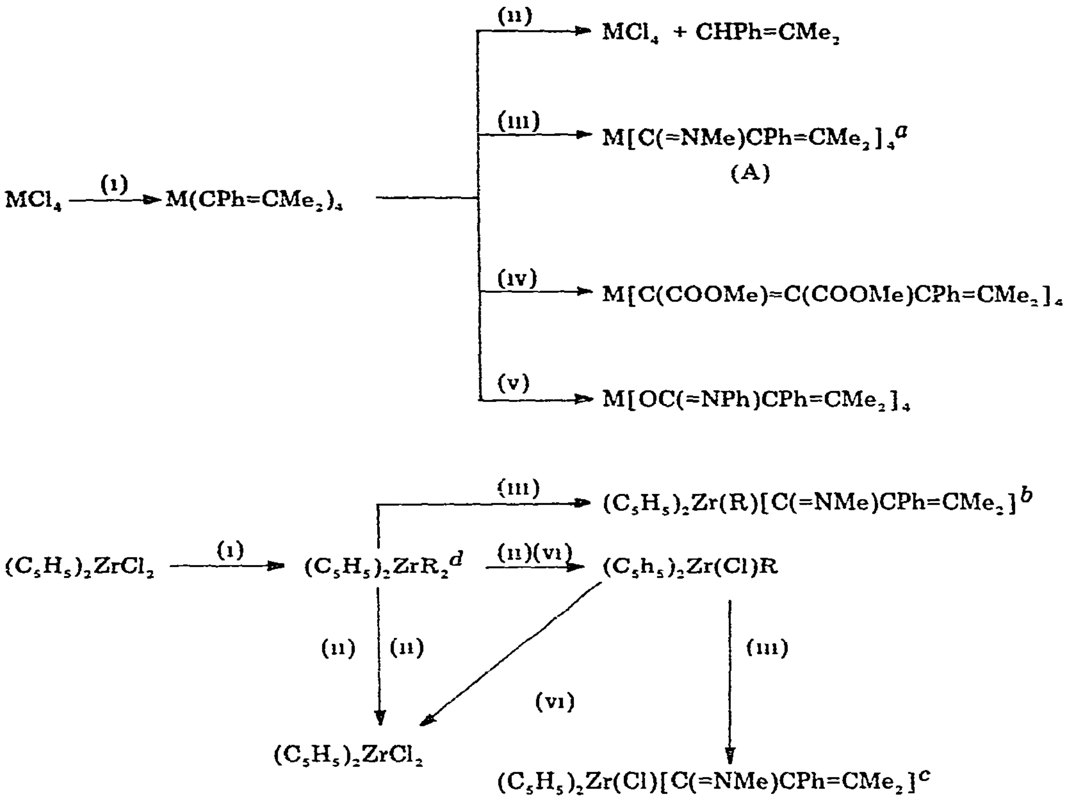

Scheme 1 (i) LiR, (R = CPh=CMe$_2$), Et$_2$O, —35° C, M = Ti, Zr, Hf (ii) HCl, CHCl$_3$, 25° C, M = Ti, Zr, Hf (iii) MeNC, benzene, 25° C, M = Zr (iv) MeOOCC≡CCOOMe, benzene, 25° C M = Zr (v) PhNCO, benzene, 25° C, M = Zr (vi) $h\nu$ ($\lambda > 390$ nm), CDCl$_3$, 25° C

NMR data chemical shift (δ ppm) relative to internal TMS, in C$_6$D$_6$, multiplicity (relative peak areas), assignment (a) 1 64 s(3), 1 80 s(3), CMe$_2$, 2 76 s(3), Me(N=C), 2 complex multiplets (5), Ph (b) 1 16 s(3), 1 44 s(3), CMe$_2$ of Zr—R, 1 73 s(3), 1 96 s(3), 2 00 s(3), CMe$_2$ and Me(N=C) of ZrC(=NMe)R, 5 51 s(10), C$_5$H$_5$, 7 16 m(10), Ph (c) 1 90 s(3), 1 77 s(3), CMe$_2$, 2 99 s(3), Me(N=C), 5.74 s(10), C$_5$H$_5$ 7 35 m(5), Ph (d) Also Ti analogue, see Table 1

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