Transalkenylations using Tin Reagents: a General Method for the Preparation of σ-Alkenyl(halogeno) Derivatives of the Early Transition Metals, and of the First Alkenyl Derivative of Scandium

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Summary The new species MR_nCl_m [M = Sc, Ti, Zr, Hf, Nb, Ta, Mo, or W; R = CPh=CMe$_2$; n = 1 (or 2 in some cases)] have been prepared from Me_3SnR or SnR_4 and appropriate halides in a clean, room temperature reaction.

Reaction of the d^0 chlorides MCl_x of Sc, Ti, Zr, Hf, Nb, Ta, and W, and of $MoCl_5$ with $SnMe_3R$ proceeds smoothly at room temperature in chloroform affording the first mixed chloro(alkenyl) transition metal species (without other ligands) stable at ambient temperature and above. Details of the reactions, which have been conveniently followed by n.m.r. spectroscopy, are shown in the Table, which gives the stoicheiometries, products, and n.m.r. characterisation for the new compounds. These species do not appear to be accessible using lithium alkenyls as alkenylating agents, despite the ready preparation of the homoleptic species by this route.[1]

Table[a]

Metal halide	Product	δ (New olefinic methyl protons)[b]
$ScCl_3$·3thf[c,d]	$ScCl_2R$·3thf	1·768[f]
$TiCl_4$[d]	$TiCl_3R$	1·685, 1·877
$ZrCl_4$[d]	$ZrCl_3R$	1·588, 1·876
$HfCl_4$[d]	$HfCl_3R$	1·594, 1·881
$NbCl_5$[d]	$NbCl_4R$	1·704, 2·088
$TaCl_5$[d]	$TaCl_4R$	1·701, 2·084
$TaCl_5$[e]	$TaCl_4R$	1·701, 2·084
WCl_6[d]	g	1·750, 2·009

[a] Throughout the Table, R represents CPh=CMe$_2$. [b] Chemical shifts of the olefinic methyls of the new compounds in $CDCl_3$ in in p.p.m. downfield from Me_4Si internal standard. [c] In line with observed reactivity trends, $ScCl_3$ was not alkenylated in two days at 20 °C. This may be a solubility effect, as (chloroform soluble) $ScCl_3$·3thf was readily alkenylated under similar conditions. thf = tetrahydrofuran. [d] Treated with Me_3SnR, δ(olefinic methyls) 1·622 and 1·921 p.p.m. (C. J. Cardin, D. J. Cardin, J. M. Kelly, D. J. H. L. Kirwan, R. J. Norton, and A. Roy, *Proc. Roy. Irish Acad.*, 1978, **77**, 365). [e] Treated with SnR_4, δ(olefinic methyls) 1·313 and 1·377 p.p.m. (see ref. in footnote d). [f] The other olefinic methyl was masked by a thf multiplet. Both the multiplets due to co-ordinated thf were shifted upfield on alkenylation: δ 2·025 and 4·371 to 1·970 and 4·188. [g] See discussion.

Previous reports of tin organylating reagents relate only to the transfer of ultimately π-bonding ligands such as cyclopentadienyl,[2] or to platinum metals.[3] Transfer of methyl groups from tin to tungsten has also been studied, but the reaction does not afford the reported products in our hands[4] (see below). The reactions [equation (1)] show a great variety in rate, *viz.* Mo $\sim$ W > Nb $\sim$ Ta > Ti $\sim$ Zr $\sim$ Hf > Sc. The Group 6 chlorides are essentially alkenylated

$$MCl_x + Me_3SnCPh{=}CMe_2 \rightarrow MCl_{x-1}R + Me_3SnCl \qquad (1)$$

after 15 min, while the Group 4A reactions require *ca.* 20 h for completion at 20 °C. Thus, addition of Me_3SnR to $TiCl_4$ (2 : 1) at 20 °C in $CDCl_3$ showed little change after mixing, but after 20 h signals (see Table) due to $TiCl_3R$ and Me_3SnCl in 1 : 1 ratio were observed, together with 1 mol of unchanged Me_3SnR which did not effect further transalkenylation. N.m.r. integration between starting material, transition metal product, and tin product establishes the stoicheiometry of the reaction and formulation of the new species beyond doubt. We have isolated $TiRCl_3$ and are currently working on the isolation of other new alkenyls.†

The new compounds are extremely sensitive to water and other protic reagents, and appear to be more thermally stable than the only previously reported mixed halogeno-derivative, $TiCl_3CH{=}CH_2$,[5] which is said to decompose above −30 °C. By contrast, the thermal stability of $TiCl_3R$ was found to be considerable, surviving without decomposition for 3 h at 65 °C and for 0·5 h at 80 °C. The other derivatives have similar thermal stabilities, and

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† Analytical data on $TiRCl_3$ and other new compounds will be reported in a full paper.

certainly survive for long periods at 20 °C, but whether this is conferred by the kinetically stabilising effects of the alkenyl substituents is difficult to assess at present.[6]

With WCl_6 both alkenyl and methyl transfer is observed, and the reaction was not easily interpreted. With the homoleptic species SnR_4 and $SnMe_4$ organylations were observed, but the products could not be unambiguously identified. It is, however, clear that even with $SnMe_4$ the reaction is by no means simple; the products including Me_2SnCl_2 (but no Me_3SnCl) and MeCl, the latter presumably formed by reductive elimination from a WCl_nMe_{6-n} species.

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