Ziegler-type Systems as Catalysts for Hydrosilylation: Linear Dimerisation with Terminal Acetylenes

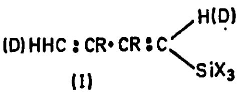
By M. F. Lappert* and S. Takahashi

(*School of Molecular Sciences, University of Sussex, Brighton* BN1 9QJ)

Summary Ziegler-type systems, $M(acac)_n$–$AlEt_3$ (M = Ni, Co, Fe) catalyse the hydrosilylation of 1,3-dienes; with $RC{\vdots}CH$, hydrosilylation is accompanied by linear dimerisation to give $CH_2{:}CR{\cdot}CR{:}CHSiX_3$ as the major product.

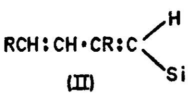
HYDROSILYLATION, the addition of X_3Si-H to unsaturated hydrocarbons, is of importance in the silicone industry and the preferred catalyst is H_2PtCl_6, Speier's catalyst.[1] We now report on the use of two-component Ziegler catalysts in hydrosilylation. With terminal acetylenes and 1,3-dienes especially there are distinctive features which may prove to be of value.

The systems $Ni(acac)_2$ or $Co(acac)_3$ with $AlEt_3$ showed only low activity towards α-olefins, such as oct-1-ene, because of competing olefin isomerisation and reduction to metal. For penta-1,3-diene, the product of 1,4-addition predominates (*e.g.*, see Table 1), whereas certain Ni^0 and Pd^0 catalysts give coupled adducts with linear 1,3-dienes, *e.g.*, $(C_4H_6)_2HSiX_3$ from C_4H_6.[2] $Ni(acac)_2$–$AlEt_3$ is the reagent of choice in terms of both activity and selectivity and is more active than Speier's catalyst.[3] Penta-1,3-diene gave $EtCH{:}CHCH_2SiX_3$ with the Ziegler system, whereas the Pt catalyst affords $MeCH{:}CH(Me)SiX_3$.[4] Isoprene yields $MeCH{:}C(Me)CH_2SiX_3$ in each case.



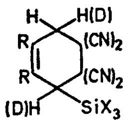
$$(D)HHC{:}CR{\cdot}CR{:}C\begin{matrix}H(D)\\ SiX_3\end{matrix}$$

(I)



$$RCH{:}CH{\cdot}CR{:}C\begin{matrix}H\\ SiX_3\end{matrix}$$

(II)



(III)

TABLE 1. *Hydrosilylation of dienes at* 20°C.

$M(acac)_n$[a]	Diene[a]	Silane[a]	Time (t/h)	Yield (%)[b] of 1,1-adduct
$Ni(acac)_2$	isoprene	$HSi(OEt)_3$; $HSiEt_3$	2	94[c]; 97[c]
$Co(acac)_3$; $Fe(acac)_3$	isoprene	$HSi(OEt)_3$; $HSiEt_3$	6; 2	44; 41
$Ni(acac)_2$	pentadiene	$HSi(OEt)_3$; $HSiEt_3$; $HSiMeCl_2$	3	96;[d] 99;[c] 96[c]

[a] $M(acac)_n$, 0·1 mmol; $AlEt_3$, 0·2 mmol (Ni) or 0·3 mmol (Fe or Co); diene, 15 mmol; and $HSi(OEt)_3$, 5·4 mmol, or $HSiEt_3$, 6·3 mmol, or $HSiMeCl_2$, 9·6 mmol. [b] Based on silane. [c] Containing a small amount of isomer(s). [d] Containing about 30% of $MeCH{:}CH{\cdot}CHMeSi(OEt)_3$.

TABLE 2. *Hydrosilylation of pent*-1-*yne at* 20 °C.

Catalyst[a]	Molar ratio[b]	Pentyne (mmol)	Silane	Silane (mmol)	Time (*t*/h)	Yield[c] (%)	Isomer ratio (I) : (II)
$Ni(acac)_2$–$AlEt_3$[d]	2	15	$HSi(OEt)_3$	5·4	3	89	81 : 19
$Ni(acac)_2$–$LiAlH_4$[e]	4	15	$HSiEt_3$	6·3	6	87	74 : 26
$NiCl_2$–$AlEt_3$[d]	2	15	$HSi(OEt)_3$	5·4	6	80	85 : 15

[a] Ni^{2+}, 0·1 mmol. [b] Molar ratio of reductant: Ni^{2+}. [c] Based on silane. [d] No solvent. [e] THF solvent.

The reaction with terminal acetylenes, such as pent-1-yne, to give mainly (I) but also (II) (see selected results in Table 2) has no precedent, 1,1-adducts having formerly been found.[5] A typical procedure was to reduce $Ni(acac)_2$ (0·5 mmol) in $n\text{-}C_3H_7C{\vdots}CH$ (90 mmol) with $AlEt_3$ (1·0 mmol), and then to add $(EtO)_3SiH$ (45 mmol) at 0°; the reaction was exothermic, and distillation gave a colourless liquid, b.p. 96—97°/1 mmHg, from which pure specimens of isomers (I) and (II) were obtained by preparative g.l.c. Evidence for structures rests on analyses, mass spectra (P^+), i.r., and ^1H n.m.r. (including decoupling experiments) spectroscopy, and a Diels–Alder reaction [(I) → (III)], as well as on similar data on the major product (I) from $n\text{-}C_3H_7\text{-}C{\vdots}CD$. When X = EtO and R = Pr^n, (III), m.p. 95—96°, was obtained (60%). The hydrosilylation products both from 1,3-dienes and terminal acetylenes are probably obtained stereoselectively, neither g.l.c. or ^1H n.m.r. suggesting that there is a mixture of isomers; however, we are unable at present to assign stereochemistry.

The nickel catalyst was inactive for internal acetylenes such as hex-2-yne or oct-4-yne. Fe^{III} and Co^{III} acetylacetonates gave polymeric products from pent-1-yne, and Cr^{III} and Mn^{II} analogues were ineffective for 1,3-dienes as well as acetylenes.

Low oxidation-state nickel compounds are usually oligo- or poly-merisation catalysts for terminal acetylenes.[6] However, hydrosilylation using a Ziegler system may prove to be a forerunner for other catalytic addition reactions of terminal acetylenes to yield coupled products.

We thank the S.R.C. for their support.

(*Received*, 21*st August* 1972; *Com.* 1460.)

---

[1] *Cf.* C. S. Cundy, B. M. Kingston, and M. F. Lappert, *Adv. Organometallic Chem.*, 1972, **11**, 253.

[2] *E.g.*, S. Takahashi, T. Shibano, H. Kojima, and N. Hagihara, *Organometallics in Chem. Synthesis*, 1970/1972, **1**, 193.

[3] I. Shiihara, W. F. Hoskys, and H. W. Post, *J. Org. Chem.*, 1961, **26**, 4000.

[4] V. F. Mironov and V. V. Nepomnina, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1960, 1419.

[5] *Cf.* C. Eaborn and R. W. Bott, in 'Organometallic Compounds of the Group IV Elements,' ed. A. G. McDiarmid, vol. 1, part 1, 1968, p. 269.

[6] *Cf.* C. W. Bird, 'Transition Metal Intermediates in Organic Synthesis,' Academic Press, New York, 1967, p. 1.