Carbon–Carbon Insertion Reactions into Metal–Nitrogen Bonds

By G. CHANDRA, T. A. GEORGE, and M. F. LAPPERT
(*The Chemical Laboratory, University of Sussex, Brighton*)

HYDROMETALLATION of olefins or acetylenes is well known. By contrast, amido-derivatives of metals or metalloids (*e.g.*, $\mathrm{LM{\cdot}NMe_2}$, where L represents the sum of all ligands other than one $\mathrm{NMe_2}$ group attached to the metal or metalloid M) have not previously been observed to react in the sense of reactions (1) and (2).[1]

$$\mathrm{LM{\cdot}NMe_2 + RC\vdots CR' \rightarrow LM{\cdot}C(R){:}C(R'){\cdot}NMe_2} \qquad (1)$$

$$\mathrm{LM{\cdot}NMe_2 + RR'C{:}CR''R''' \rightarrow LM{\cdot}C(R,R'){\cdot}C(R'',R'''){\cdot}NMe_2} \qquad (2)$$

It is now found that the presence of powerfully electron-withdrawing groups in the hydrocarbon often makes possible such reactions even under quite mild conditions. Thus, it appears that the driving force is nucleophilic attack by $\mathrm{LM{\cdot}\ddot{N}Me_2}$. Formally related CC insertion reactions are with $\mathrm{R_3Sn{\cdot}OR'/EtO_2CC\vdots C{\cdot}CO_2Et}$,[2] and with $\mathrm{Ph_3Sn{\cdot}PPh_2/CH_2{:}CH_2}$ (or $\mathrm{PhCH{:}CH_2}$, or $\mathrm{CH_2{:}CH{\cdot}CH_2Cl}$);[3] the latter are, however, free-radical initiated.

The reaction conditions, to obtain the products shown in the Table, were never more severe than the refluxing of reagents at 35—60° in diethyl ether or light petroleum. All the adducts are new and analyse satisfactorily. Infrared, n.m.r., and mass-spectral data are available; these show that some of the compounds (especially that of Ti) are chelated, and that they are probably (for the acetylenic adducts) products of *cis*-addition.

The synthesis of a stable σ-organotitanium compound is noteworthy, but mixing of reagents at $-78°$ was necessary. At room temperature, even a trace of $\mathrm{Ti(NMe_2)_4}$ caused the polymerisation or polycondensation of the acetylenedicarboxylic ester (see ref. 4 for related reactions with organic bases). With the olefinic substrates, (high) polymerisation takes place with $\mathrm{CH_2{:}CH{\cdot}CN}$ (as already observed[5]) but less readily with $\mathrm{CH_2{:}C(Me){\cdot}CN}$. These are probably multistep molecular insertions (rather than anionic processes[5]), and may have mechanistic similarity to the recently described selective radical polymerisations using $\mathrm{Mn^{III}(facac)_3}$ [facacH = $\mathrm{CF_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_3}$].[6] Catalyst reactivity decreases in the series $\mathrm{Ti(NMe_2)_4 > Zr(NMe_2)_4 > (\pi\text{-}C_5H_5)_2Zr(NMe_2)_2}$ [the last named compound (subliming at 120°/0·1 mm.) was obtained from $\mathrm{Zr(NMe_2)_4/C_5H_6}$; (*cf.* ref. 7): $\mathrm{Ti(NMe_2)_4 + C_5H_6 \rightarrow Me_2NH + (\pi\text{-}C_5H_5)Ti(NMe_2)_3}$]. In the tin series, multistep insertion, to give $\mathrm{Et_3Sn{\cdot}[CH(CHO)\text{-}CH_2]_n{\cdot}NMe_2}$ ($n \sim 6$), was observed in only one instance.

Reactions with related reagents which take a different path are shown in (3)—(6). Examples of conversions of $\mathrm{>C{:}O \rightarrow >C(NMe_2)_2}$,[8] and $\mathrm{-CO_2R \rightarrow -CO{\cdot}NMe_2}$,[9] using amides of Ti or Sn, have recently been reported. Reaction (3) is particularly interesting and may prove valuable for the synthesis of enamines. Phenyl acetate behaves like ethyl acetate, giving $\mathrm{AcNMe_2}$ and $\mathrm{Me_3SnOPh}$.

$$\mathrm{Me_3SnNMe_2 + AcOCH{:}CH_2 \rightarrow Me_3SnOAc + Me_2NCH{:}CH_2 \rightarrow polymer} \qquad (3)$$

$$\mathrm{Me_3SnNMe_2 + CH_2{:}CMe{\cdot}CO_2Me \rightarrow Me_3SnOMe + CH_2{:}CMe{\cdot}CO{\cdot}NMe_2} \qquad (4)$$

TABLE

Adduct (Yield, %)	B.p. (°/mm.)	Adduct (Yield, %)	B.p. (°/mm.)
$\mathrm{Me_3SiC(CO_2Et):C(CO_2Et)\cdot NMe_2}$[a] (72)	100/0·01	$\mathrm{Et_3SnCH(CN)\cdot CH_2\cdot NMe_2}$[d] (69)	97/0·02
$\mathrm{Me_3GeC(CO_2Et):C(CO_2Et)\cdot NMe_2}$[a] (78)	80/0·02	$\mathrm{Me_3SnC(Me)(CN)\cdot CH_2\cdot NMe_2}$[e] (54)	78—80/0·02
$\mathrm{Me_3SnC(CO_2Et):C(CO_2Et)\cdot NMe_2}$[a](98)	100/0·02	$\mathrm{Et_3SnCH(CO_2Me)\cdot CH\cdot NMe_2}$[f] (93)	88/0·02
$\mathrm{B[C(CO_2Et):C(CO_2Et)\cdot NMe_2]_3}$[a] (83)	12/0·03	$\mathrm{Et_3SnCH(CHO)\cdot CH_2\cdot NMe_2}$[g] (99)	86/0·03
$\mathrm{MeO(Me_2N)_2TiC(CO\cdot NMe_2):C(CO_2Me)\cdot NMe_2}$[b] (55)	m.p. 58° (d.)	$\mathrm{Et_3SnCH(CHO)\cdot CH(Me)\cdot NMe_2}$[h] (95)	80/0·01
$\mathrm{(MeO)_2Zr[C(CO\cdot NMe_2):C(CO_2Me)\cdot NMe_2]_2}$[b] (23)	m.p. > 240°(d.)	$\mathrm{Et_3SnCH(CHO)\cdot CH(Ph)\cdot NMe_2}$[i] (88)	69—71/0·02
$\mathrm{Me_3SnCCl:CPh\cdot NMe_2}$[c] (40)	60—89/0·04 (d).		

[a] From $\mathrm{EtO_2C\cdot C\vdots C\cdot CO_2Et/LM\cdot NMe_2}$
[b] From $\mathrm{MeO_2C\cdot C\vdots C\cdot CO_2Me/M(NMe_2)_4}$
[c] From $\mathrm{PhC\vdots CCl/Me_3SnNMe_2}$
[d] From $\mathrm{CH_2:CH\cdot CN/Et_3SnNMe_2}$
[e] From $\mathrm{CH_2:C(Me)\cdot CN/Me_3SnNMe_2}$
[f] From $\mathrm{CH_2:CH\cdot CO_2Me/Et_3SnNMe_2}$
[g] From $\mathrm{CH_2:CH\cdot CHO/Et_3SnNMe_2}$
[h] From $\mathrm{MeCH:CH\cdot CHO/Et_3SnNMe_2}$
[i] From $\mathrm{Ph\cdot CH:CH\cdot CHO/Et_3SnNMe_2}$

$$\mathrm{PhCH{:}CH\cdot CHO + Ti(NMe_2)_4 \rightarrow PhCH{:}CH\cdot CH(NMe_2)_2 + 1/\mathit{n}[OTi(NMe_2)_2]_\mathit{n}} \qquad (5)$$

$$\mathrm{CH_2{:}CH\cdot CO_2H \xrightarrow{Ti(NMe_2)_4} (CH_2{:}\,CH\cdot CO\cdot NMe_2)_\mathit{n}} \qquad (6)$$

(*Received, December 21st,* 1966; *Com.* 1021.)

---

[1] M. F. Lappert and B. Prokai, *Adv. Organometallic Chem.*, 1966, **5**, 225.
[2] I. F. Lutsenko, S. V. Ponamarev, and O. P. Petrii, *J. Gen. Chem.* (*U.S.S.R.*), 1962, **32**, 886.
[3] H. Schumann, P. Jutzi, and M. Schmidt, *Angew. Chem.*, 1965, **77**, 912.
[4] O. Diels, *Ber.*, 1942, **75***B*, 1452; R. M. Acheson and G. A. Taylor, *J. Chem. Soc.*, 1960, 1691.
[5] E. Perry, *Makromol. Chem.*, 1963, **65**, 145.
[6] C. H. Bamford and D. J. Lind, *Chem. Comm.*, 1966, 792.
[7] G. Chandra and M. F. Lappert, *Inorg. Nuclear Chem. Letters*, 1965, **1**, 83.
[8] H. Weingarten and W. A. White, *J. Org. Chem.*, 1966, **31**, 2874.
[9] T. A. George and M. F. Lappert, *Chem. Comm.*, 1966, 463.