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ACTIVATION OF TRANSITION METAL–ALKYL BONDS IN METHYL TITANIUM TRICHLORIDE, DIALKYL(BIPYRIDINE)NICKEL AND OTHER TRANSITION METAL ALKYLS BY INTERACTION WITH ORGANOALUMINUM COMPOUNDS

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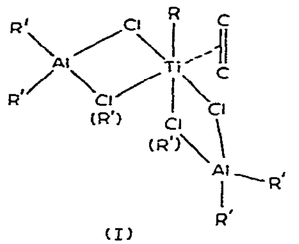
SUMMARY

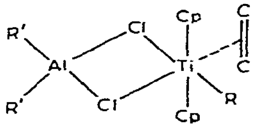
Metal–carbon bonds of various alkyl–transition metal compounds including $TiCH_3Cl_3$, NiR_2Bipy, $Cr(C_2H_5)Cl_2Py_3$, FeR_2Bipy_2, $CuCH_3(PPh_3)_3(C_6H_5CH_3)$ are activated and split on interaction with organoaluminum compounds [AlR'_3 and $AlR'_2(OC_2H_5)$, where $R'=CH_3$, C_2H_5, and n-C_3H_7]. Kinetics of the cleavage of the Ti–CH_3 bond in $TiCH_3Cl_3$ and Ni–R bonds in NiR_2Bipy in solutions containing the organoaluminum compounds were studied by volumetric and spectroscopic methods, respectively. In both cases the reactions were first order with respect to the concentrations of the alkyl–transition metal compounds. The pseudo first order rate constants for the decomposition of NiR_2Bipy in THF solution on addition of AlR'_3 were proportional to $[AlR'_3]$ for low concentrations of AlR'_3 and to $1/[AlR'_3]$ for high concentrations. Based on the kinetics, a mechanism is proposed which involves coordination of AlR'_3 with NiR_2Bipy, and splitting the Ni–R bonds of the binuclear adduct thus formed. The decrease of the rate constants at higher concentrations of AlR'_3 is attributed to displacement of the complexed organoaluminum component by interaction with $AlR'_3 \cdot THF$.

Despite the great amount of effort devoted to elucidating the reaction mechanism of Ziegler-type polymerization, the role of organoaluminum compounds in the mixed catalyst systems still remains uncertain. It has been clearly established that alkylaluminum compounds act as alkylating and reducing agents towards transition metal compounds[1,2], but the aluminum-free transition metal alkyls isolated from the reaction mixtures of transition metal compounds and the alkylaluminum compounds often show less, and sometimes negligible, activities for olefin polymerization compared with those of the mixed catalyst systems. Methyltitanium trichloride serves as an excellent example of isolated transition metal alkyls which do not exhibit activity for olefin polymerization in the pure state, and it is known that the polymerization activity of methyltitanium trichloride develops on addition of organoaluminum compounds or titanium trichloride[1c].

Several binuclear models composed of transition metal alkyls and organoaluminum components as shown below have been proposed as models of the active species in the Ziegler catalysts[3-5].



(I)



(II)

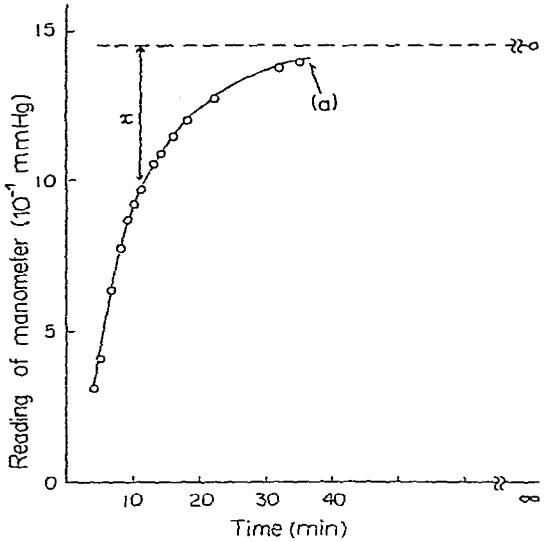
In these binuclear models the active centers for the polymerization are regarded as the transition metal alkyls toward which the monomers coordinate and are inserted between the metal–carbon bonds. The organoaluminum components are considered to modify the reactivity of the transition metal alkyl center through the bridging halogen atoms or R′ groups. If these binary models are valid, we think that there are two effects of the organoaluminum component: (*i*) as a modifier of the stability of the transition metal–alkyl (M–R) bond, and hence the activity towards insertion of monomer between the M–R bond, (*ii*) as modifier of the reactivity of the transition metal complex toward olefin. These two factors may sometimes act cooperatively and sometimes competitively. If we regard the organoaluminum compounds as Lewis acids, the organoaluminum component may withdraw electrons from the transition metal alkyl, thus leading to activation of the M–R bond[6], but too much destabilization of the M–R bond would destroy the catalyst activity. The decrease in the electron density of the transition metal component may result in an enhancement of the interaction with the olefin if σ-donation from the olefin to the metal is the main factor in determining the metal–olefin interaction[7] or may lead to a decrease of the interaction with the olefin if the back donation from metal to olefin is the decisive factor in determining the extent of interaction[6,8].

In actual catalyst systems these two factors are intertwined and difficult to separate, and somewhat speculative theories have been developed which are based mainly on indirect evidence. We expected that more direct information concerning the first factor could be obtained by studying the interaction of isolated transition metal alkyls with organoaluminum compounds and in fact, we have observed striking activation of M–R bonds in the presence of organoaluminum compounds. The effect of organoaluminum compounds on the stabilities of transition metal alkyl complexes also has important implications for conditions of preparation of transition metal alkyls. These complexes are often conveniently prepared by reactions of transition metal halides or acetylacetonates with organoaluminum compounds. The present results indicate that care should be taken in choosing the ratio of the organoaluminum compound to the transition metal compound, the reaction temperature, and the work-up procedure.

RESULTS AND DISCUSSION

(*i*). *Activation of Ti–CH_3 bond in $TiCH_3Cl_3$*

The cleavage reactions of the Ti–CH_3 bond in $TiCH_3Cl_3$ in toluene solution in



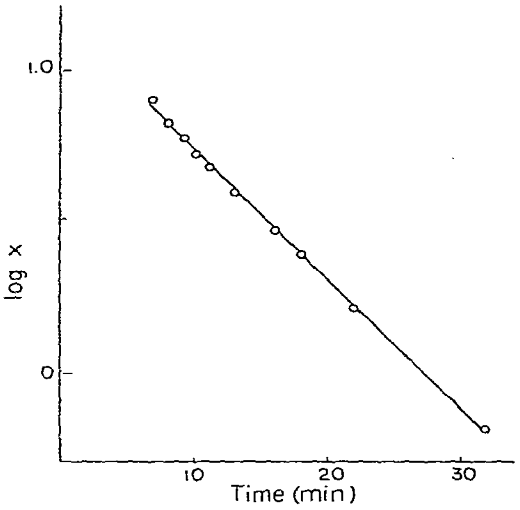


Fig. 1. Evolution of CH_4 from the $TiCH_3Cl_3/Al(C_2H_5)_3$ system at $-14.5°$. $TiCH_3Cl_3=0.68$ g, $Al(C_2H_5)_3=0.12$ ml, and toluene = 9.2 ml.

Fig. 2. A plot of log x against time, based on data shown in Fig. 1.

the presence of $Al(C_2H_5)_3$ and $Al(n\text{-}C_3H_7)_3$ were followed by measuring the amounts of gas evolved at low temperatures, at which the decomposition of $TiCH_3Cl_3$ is negligible in absence of trialkylaluminum compounds. The gas evolved was composed of methane and ethane in ratios of 100/1 to 20/1 in the case of $Al(C_2H_5)_3$. The final amount of the gas evolved was 85–90% of the theoretical. The plot of the logarithms of the volume, x, of evolved gas against time gave a straight line, as shown in Fig.1, indicating first order dependence on the concentration of $TiCH_3Cl_3$ (Fig. 2).

$$\frac{-d[TiCH_3Cl_3]}{dt} = k_{Ti}[TiCH_3Cl_3] \tag{1}$$

The pseudo-first-order rate constant k_{Ti} was roughly proportional to the concentration of organoaluminum compound (Table 1).

On variation of the organoaluminum compounds the rate constant k_{Ti} increases in the order $Al(C_2H_5)_2(OC_2H_5) < Al(n\text{-}C_3H_7)_3 < Al(C_2H_5)_3$, indicating that the stronger is the Lewis acidity of the organoaluminum, the more strongly is the Ti–CH_3 bond activated. In the case of $Al(C_2H_5)_3$ the activation energy was roughly estimated as 11 kcal/mol. The activation energy is somewhat smaller than that (19.6 kcal/mol) obtained by Dyachkovsky *et al.*[9] for the decomposition of $TiCH_3Cl_3$ on interaction with tetrahydrofuran.

After completion of the reaction below $-5°$ in toluene, $TiCl_3$ was obtained as a brownish purple precipitate. The evolved gas was mainly methane, whereas the gases evolved in reactions carried out at room temperature contained larger amounts of alkanes originating from the organoaluminum compounds, suggesting that some alkyl exchange reactions take place between the titanium and the aluminum com-

TABLE 1

THE RATE CONSTANT k_{Ti} FOR THE DECOMPOSITION OF $TiCH_3Cl_3$ ON REACTION WITH ORGANOALUMINUM IN TOLUENE

Organoaluminum	*Temperature (°C)*	*Concentration of organoaluminum (mol/l)*	$k_{Ti} \times 10^2$ *(min⁻¹)*
$Al(C_2H_5)_3$	−5	0.046	9.1
		0.085	17
	−14.5	0.041	5.2
		0.046	4.9
		0.097	7.7
		0.11	7.4
		0.15	13
	−30	0.069	1.2
		0.13	2.6
$Al(n\text{-}C_3H_7)_3$	−13	0.038	2.3
		0.065	4.7
		0.21	16.2
$Al(C_2H_5)_2(OC_2H_5)$	−5	0.092	4.0

ponents at room temperature. When the reaction was carried out in tetrahydrofuran (THF) at −78° a brown precipitate was gradually formed with evolution of almost pure methane, and $TiCl_3(THF)_3$, identified by elemental analysis and IR spectroscopy, was recovered from the reaction system after the latter had been left at room temperature. The rate of the decomposition of $TiCH_3Cl_3$ in the presence of organoaluminum compounds in tetrahydrofuran at low temperatures (below −10°) was much smaller than in toluene. The source of the hydrogen which appears in the methane in the decomposition of $TiCH_3Cl_3$ has been discussed by de Vries[10] and Dyachkovsky *et al.*[9]. De Vries considered the methyl group of $TiCH_3Cl_3$ as the most likely source. However, since the amount of CH_4 evolved accounts for 90% of $TiCH_3Cl_3$ present in the system, the solvent appears to be the most probable hydrogen source, although no further attempt was made to establish this.

(ii). *Activation of Ni–alkyl bonds in* NiR_2Bipy

Since NiR_2Bipy absorbs in the visible region and dimethyl- and diethylnickel complexes are quite stable at room temperature, the decomposition of NiR_2Bipy in the presence of AlR'_3 was conveniently followed by a spectroscopic method. The decomposition of NiR_2Bipy takes different routes depending on the solvent. In nonpolar solvents such as benzene, toluene and hexane, rapid decomposition of NiR_2-Bipy occurs with evolution of gas mainly composed of RH coming from the nickel complexes. The spectral change indicates the formation of AlR'_3–Bipy adducts. Wilke and Misbach[11] have investigated the decomposition of $Ni(CH_3)_2Bipy$ in toluene solution containing AlR'_3, and they explained the destabilization of $Ni(CH_3)_2$-Bipy in terms of displacement of the stabilizing dipyridyl ligand through adduct formation with the acidic trialkylaluminums.

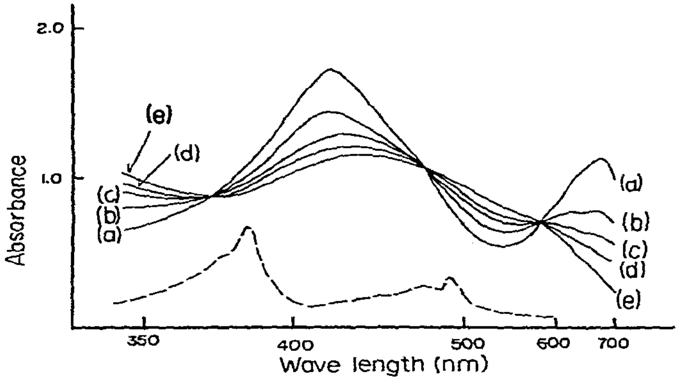


Fig. 3. The change of the spectrum in the reaction of $Ni(C_2H_5)_2Bipy$ with $Al(C_2H_5)_3$ in THF at 29.7°. $[Ni(C_2H_5)_2Bipy]_0 = 5.6 \times 10^{-4}$ mol/l. $[Al(C_2H_5)_3] = 0.117$ mol/l. Time (sec) = (a) 0, (b) 195, (c) 395, (d) 592 and (e) ∞. The broken line indicates the spectrum of the 2,2'-bipyridine-$Al(C_2H_5)_3$ adduct ([Bipy] = 4.5×10^{-5} mol/l).

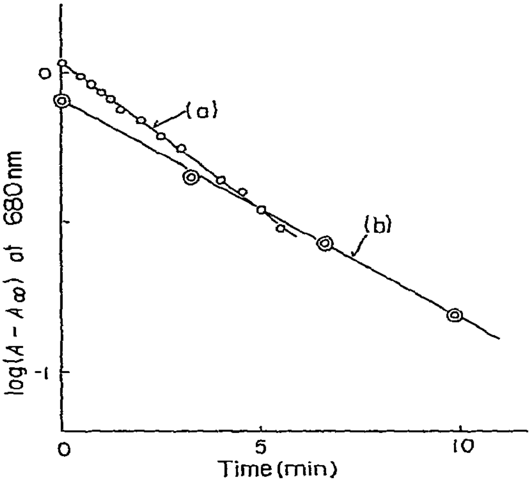


Fig. 4. Reaction of $Ni(C_2H_5)_2Bipy$ with $Al(C_2H_5)_3$ in THF at 29.5°, $\text{Log}(A - A_\infty)$ vs. Time (A: absorbance at 680 nm). $[Al(C_2H_5)_3]$ = (a) 0.0983 mol/l, and (b) 0.117 mol/l.

On the other hand, in polar solvents such as tetrahydrofuran, dimethylformamide and acetonitrile, the spectra of the solutions containing NiR_2Bipy change, with clear isosbestic points (Fig. 3), and the characteristic absorption bands of AlR'_3–bipyridine adducts were not observed except when high concentrations of AlR'_3 were employed ($[AlR'_3] > 1$ mol/l in THF). The rate was measured by observing the decrease of the absorbance at 680 nm, and the reaction was found to be of first order with respect to the concentration of NiR_2Bipy ($R = CH_3, C_2H_5$) in THF (Fig. 4).

$$-\frac{d[NiR_2Bipy]}{dt} = k_{Ni}[NiR_2Bipy] \tag{2}$$

The pseudo first order rate constant k_{Ni} for the decomposition of $Ni(C_2H_5)_2$-Bipy increases linearly with the concentration of AlR'_3 in a lower concentration range

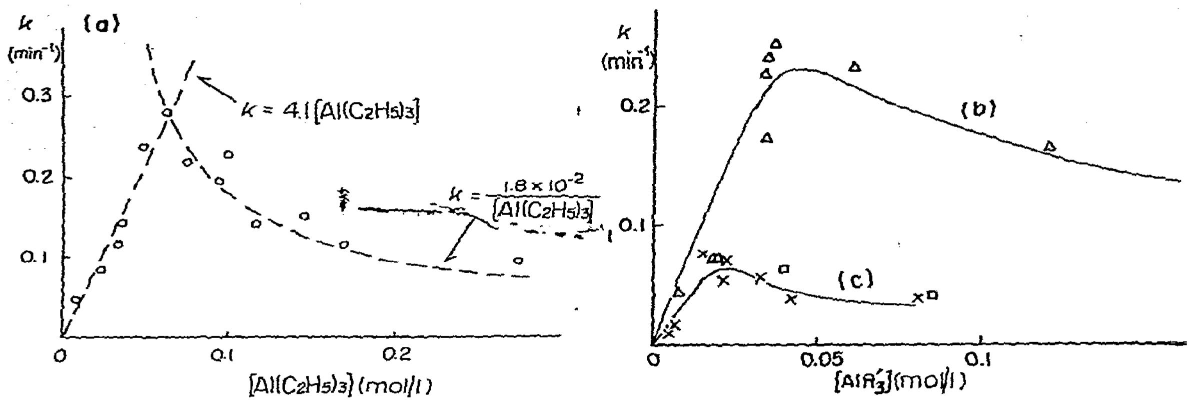


Fig. 5. Pseudo first order rate constant k_{Ni} against the concentration of AlR_3 for the reaction of $Ni(C_2H_5)_2Bipy$ with (a) ○ $Al(C_2H_5)_3$ at 29.5°, (b) × $Al(C_2H_5)_3$ at 19.0°, (c) △ $Al(n\text{-}C_3H_7)_3$ at 31.6°, and (d) □ $Al(CH_3)_3$ at 31.2°.

in which $[AlR'_3]$ ($R' = CH_3, C_2H_5, n\text{-}C_3H_7$) is below about 5×10^{-2} mol/l, and then at higher concentrations decreases at a rate inversely proportional to the concentration of AlR'_3, as shown in Fig. 5.

The linear increase of k_{Ni} with the concentration of AlR'_3 can be explained by complexing of AlR'_3 with the alkylnickel complex and resultant activation of Ni–R bonds by the electron withdrawal from the nickel to the aluminum component. The decrease of k_{Ni} at higher concentrations of AlR'_3 is more difficult to explain.

In order to explain the kinetic behavior we suggest the following mechanism:

$$\underset{\text{(III)}}{NiR_2Bipy \cdot THF} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{(IV)}}{NiR_2Bipy} + THF \tag{3}$$

$$\underset{\text{(V)}}{AlR'_3 \cdot THF} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\text{(VI)}}{AlR'_3} + THF \tag{4}$$

$$\underset{\text{(IV)}}{NiR_2Bipy} + \underset{\text{(VI)}}{AlR'_3} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \underset{\text{(VII)}}{NiR_2Bipy(AlR'_3)} \xrightarrow{k_4} \text{scission of Ni–R bonds}$$

$$\underset{\text{(VII)}}{NiR_2Bipy(AlR'_3)} + \underset{\text{(V)}}{AlR'_3 \cdot THF} \xrightarrow{k_5} \underset{\text{(III)}}{NiR_2Bipy \cdot THF} + Al_2R'_6 \tag{6}$$

$$Al_2R'_6 \xrightarrow[\text{immediately}]{2THF} 2AlR'_3 \cdot THF \tag{7}$$

NiR_2Bipy is present in solution in a solvated form (III) as observed spectroscopically[6], and the trialkylaluminum is also present in a solvated form (V) as shown by the NMR spectra[12]. The solvated species (III) and (V) may release the coordinated solvent in solution at rate constants k_1 and k_2, respectively. Complexing of free AlR'_3 (VI) with the free NiR_2Bipy (IV) may lead to a binary complex (VII) in which the Ni–R bonds are destabilized by the more acidic AlR'_3 component, and bond scission would result. We did not attempt to isolate the unstable intermediate, (VII) but Misbach did isolate such an adduct from the reaction of $Ni(CH_3)_2Bipy$ with $Al(CH_3)_3$ in toluene at −78°, and proposed a binuclear structure with bridging methyl groups[11]. On the other hand some examples of direct transition metal–aluminum bonding are also known[13].

The mechanism represented by reactions (3)–(5) explains the linear dependence of the rate on the trialkylaluminum concentration in the lower concentration range. The rate decrease in the higher concentration of trialkylaluminum may be explained by reaction (6), in which the complexed AlR'_3 component in (VII) is displaced by $AlR'_3 \cdot THF$ to generate (III) along with the dimeric species of trialkylaluminum, which is converted immediately to the solvated species in THF in reaction (7). The driving force for reaction (6) is the strong tendency of AlR'_3 to form the dimer and the adduct formation between THF and NiR_2Bipy.

Application of the stationary state approximation to the concentrations of (IV) and (VII), and the assumption that the scission of the Ni–R bonds is the rate determining step leads to the following rate equation:

$$-\frac{d[NiR_2Bipy \cdot THF]}{dt} = k_4 \cdot [VII]$$

$$= \frac{k_1 \cdot k_3 \cdot k_4 [AlR'_3] \cdot [NiR_2Bipy \cdot THF]}{k_3 \cdot k_5 \cdot [AlR'_3 \cdot THF] \cdot [AlR'_3] + (k_3 \cdot k_4 \cdot [AlR'_3] + k'_{-1} \cdot k_5 \cdot [AlR'_3 \cdot THF]) + k'_{-1} \cdot (k_{-3} + k_4)} \quad (8)$$

where $k'_{-1} = k_{-1} \cdot [THF]$.

Replacing $[AlR'_3]$ by $K[AlR'_3 \cdot THF]$ where K is $k_2/k_{-2} \cdot [THF]$, we obtain the following rate expression for the pseudo first order rate constant k_{Ni}:

$$k_{Ni} = \frac{k_1 \cdot k_3 \cdot k_4 \cdot K \cdot [AlR'_3 \cdot THF]}{k_3 \cdot k_5 \cdot K \cdot [AlR'_3 \cdot THF]^2 + (k_3 \cdot k_4 \cdot K + k'_{-1} \cdot k_5) \cdot [AlR'_3 \cdot THF] + k'_{-1} \cdot (k_{-3} + k_4)} \quad (9)$$

Eqn. (9) is in accordance with the observation that the pseudo first order rate constant k_{Ni} is proportional to $[AlR'_3 \cdot THF]$ when $[AlR'_3 \cdot THF]$ is small and to $1/[AlR'_3 \cdot THF]$ when $[AlR'_3 \cdot THF]$ is large.

Simulation of the experimental results shown in Fig. 5 by employing appropriate values for the rate constants in eqn. (9) was attempted. Fig. 6 compares the experimental values with the simulated curve based on the figures given in eqn. (10).

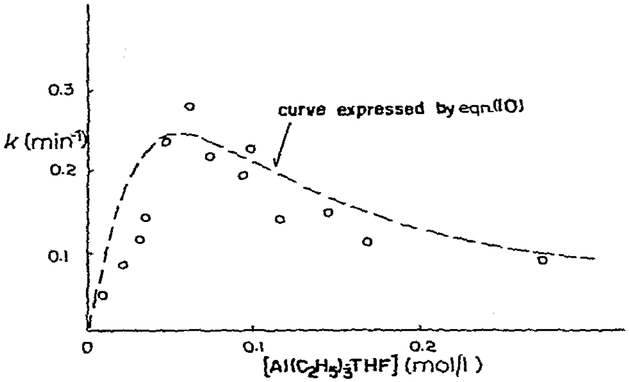


Fig. 6. Comparison of the experimental values of k_{Ni} at 29.5° with the simulated curve derived from eqn. (10).

$$k_{\mathrm{Ni}} = \frac{9.5[\mathrm{AlEt_3\cdot THF}]}{300[\mathrm{AlEt_3\cdot THF}]^2+5[\mathrm{AlEt_3\cdot THF}]+1} \qquad (10)$$

The agreement of the simulated curve with the experimental values is reasonable if we take into account the difficulties in measuring the higher rate constants, and also in determining the concentrations of $AlEt_3\cdot THF$, especially at low concentrations, because of the air-sensitivity of the triethylaluminum.

Although the spectral change of NiR_2Bipy in THF on reaction with AlR'_3 is accompanied by clear isosbestic points to almost completion of the reaction some shifts of isosbestic points were observed depending on the concentration of the AlR'_3 concentration. The spectrum of the solution after the completion of the reaction also varied with the concentrations of AlR'_3. These facts can be interpreted by assuming an equilibrium between AlR'_3 and the dealkylated nickel bipyridine species, presumably the NiBipy·solvent which we observed in the dealkylation of NiR_2Bipy in the presence of electronegative olefins[6].

$$\mathrm{NiBipy\cdot THF+AlR'_3\cdot THF} \overset{K}{\rightleftharpoons} \mathrm{NiBipy\cdot AlR'_3} \qquad (11)$$

The equilibrium constant K for reaction (11) was estimated as follows. NiBipy-(methacrylonitrile)[6] was dissolved in THF giving a green solution which turned red on addition of the triethylaluminum. (In our previous paper, NiBipy·THF was judged to be responsible for the green color[6].) The change of the color on addition of $Al(C_2H_5)_3$ was followed spectroscopically and an isosbestic point was observed for $Al(C_2H_5)_3$ concentration between 0 and 8.3×10^{-3} mol/l. From the spectral change, assuming the existence of equilibrium (11), the equilibrium constant K was estimated as 2×10^2 l/mol at 18.5°.

When NiR_2Bipy ($R=CH_3$, C_2H_5) was treated in THF with $Al(C_2H_5)_2(OC_2H_5)$ an almost identical spectral change was observed as in the reaction with AlR'_3, although the rate was smaller (Fig. 7). The reaction was again first order with respect to the concentration of NiR_2Bipy, and in the case of $Ni(C_2H_5)_2Bipy$ the

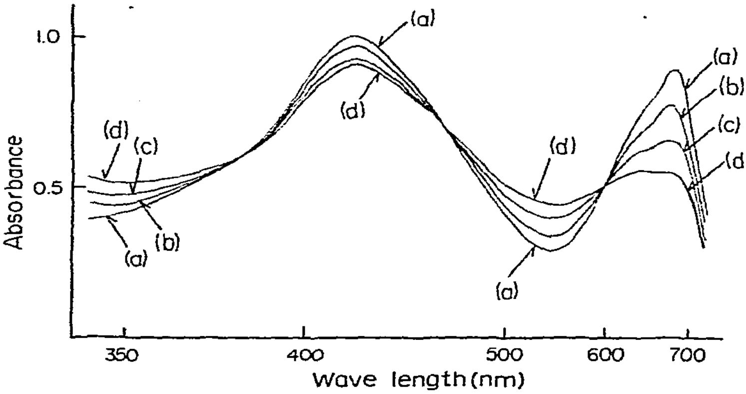


Fig. 7. The change of the spectrum in the reaction of $Ni(C_2H_5)_2Bipy$ with $Al(C_2H_5)(OC_2H_5)$ in THF at 29.7°. $[Ni(C_2H_5)_2Bipy]_0=3\times10^{-4}$ mol/l. $[Al(C_2H_5)_2(OC_2H_5)]=2.39\times10^{-2}$ mol/l. Time (min)=(a) 0 (b) 7.5, (c) 21 and (d) 87.

pseudo first order rate constant changed as found for the reaction with AlR'_3, showing a maximum at about 4×10^{-2} mol/l of $[Al(C_2H_5)_2(OC_2H_5)]$ at 29.8°.

The decomposition of $Ni(C_2H_5)_2$Bipy by $Al(C_2H_5)_2(OC_2H_5)$ was surprising, since $Ni(C_2H_5)_2$Bipy can usually be prepared in high yields by using $Al(C_2H_5)_2$-(OC_2H_5) as the alkylating agent. Probably decomposition of $Ni(C_2H_5)_2$Bipy does not occur appreciably under the usual preparative conditions because the rather narrow concentration range in which the maximum decomposition of $Ni(C_2H_5)_2$-Bipy takes place may usually be fortuitously avoided. But we did observe decomposition of $Ni(C_2H_5)_2$Bipy when the reaction system was left too long (over two days) without isolation of the $Ni(C_2H_5)_2$Bipy. The reason for the difficulty of the preparation of $Ni(C_2H_5)_2$Bipy with $Al(C_2H_5)_3$ can be also understood in the light of our results. When $AlEt_3$ is employed as the alkylating agent, the conditions necessary to avoid the decomposition of the $Ni(C_2H_5)_2$Bipy are more critical, and extra care must be taken in choosing the conditions.

Decomposition of NiR_2Bipy in THF on addition of $AlCl_3$ was extremely rapid compared with that in presence of AlR'_3; decomposition of $Ni(C_2H_5)_2$Bipy was too rapid to be followed even when only 3.3 mmol/l solution of $AlCl_3$ was used.

We previously observed that the Ni–R bonds of NiR_2Bipy are destabilized by interactions with electronegative olefins, which can be regarded as π-acids, and that the greater the acidity of the olefin, the more strongly are the Ni–R bonds activated by coordination of the olefin. We explained the activation in terms of the lowering of the energy level of the nickel d-orbitals in the presence of π-acids, which facilitates the electronic excitation from the bonding Ni–alkyl orbital. The new results indicate that the effect of aluminum compounds on the activation of Ni–R bonds increases with the increase of Lewis acidity in the order $AlR'_2(OEt) < AlR'_3 < AlCl_3$. The stronger activation of the Ni–R bonds by stronger Lewis acid can be explained as before.

(iii). *Activation of M–R bonds of other transition metal alkyl complexes*

The ethylchromium complex $Cr(C_2H_5)Cl_2Py_3$ is very stable, and no change of the electronic spectrum can be detected at room temperature in THF solution over a long period[14]. On addition of $Al(n\text{-}C_3H_7)_3$ to the THF solution at room temperature, a rapid evolution of gas was observed, and the color of the solution changed from green to black. The gas was composed mainly of ethane, but contained a small amount of propane, the proportion of which increased with time.

The methylcopper complex $CuCH_3(PPh_3)_3$(toluene)[15], which is stable at −10°, was also readily decomposed on treatment with $Al(CH_3)_3$ in toluene, the color changing from yellow to black, and methane being evolved.

The alkyliron complexes FeR_2Bipy_2[2b,16] ($R = CH_3$ and C_2H_5), which are stable at room temperature in THF, were also readily decomposed on addition of $Al(C_2H_5)_3$, with evolution of a gas composed mainly of RH derived from the transition metal alkyls.

Thus the destabilization of transition metal alkyls by interaction with organoaluminum compounds appears to be a fairly general phenomenon, although we noted a contrasting stabilization effect of organoaluminum compounds for $MnHI \cdot (THF)_{1.5}$[17].

It is noted that the decomposition of transition metal alkyls releases alkanes which are thought to be formed by hydrogen abstraction from the solvent, and only small amounts of disproportionation and coupling products of the alkyls were detected. For example NiR_2Bipy released a gas composed mainly of RH on interaction with organoaluminum compounds, and this contrasts with the decomposition of NiR_2Bipy on heating of the solid complexes or on treatment with olefins, for which some coupling and disproportionation products were always observed, depending on the nature of the alkyl groups attached to nickel[6].

EXPERIMENTAL

I. Materials

$TiCH_3Cl_3$[1c], NiR_2Bipy[2,6], FeR_2Bipy[2,16], $CuCH_3$(triphenylphosphine)$_3$-(toluene)[15] and $Cr(C_2H_5)Cl_2 \cdot 3$(pyridyine)[14] were prepared as described in the literature. Solvents were dehydrated, distilled, and stored under nitrogen. Commercially available trialkylaluminum compounds were used without further purification. Dialkylaluminum monoethoxides were prepared from trialkylaluminum compounds and ethyl alcohol and purified by distillation. Aluminum trichloride was recrystallized from THF.

II. Reactions of alkyl transition metal compounds with organoaluminums

In a typical procedure the reaction of $TiCH_3Cl_3$ with AlR'_3 was carried out as follows. To a THF (15 ml) solution of $TiCH_3Cl_3$ (1.23 g) was added 1.7 ml of Al(n-$C_3H_7)_3$. A brown precipitate formed gradually, with evolution of almost pure methane. When the mixture was left at room temperature $TiCl_3 \cdot 3THF$ was obtained. When $TiCH_3Cl_3$ was treated with AlR'_3 ($R' = C_2H_5$, n-C_3H_7) in toluene at about -5 to $-30°$, $TiCl_3$ was obtained with evolution of a gas composed mainly of CH_4 ($CH_4/R'H = 100/1 - \approx 5$). When the reactions were carried out at room temperature, the gas evolved contained comparable amounts of R'H and CH_4 at the end of the reaction.

Reactions of other alkyl transition metal compounds with organoaluminum compounds were carried out similarly.

III. Kinetics

The amount of gas evolved by cleavage of the Ti–CH_3 bond was measured by using a manometer attached to a vacuum line. The spectral change of the NiR_2Bipy/AlR'_3 or $NiR_2Bipy/AlR'_2(OC_2H_5)$ system was followed with a Shimadzu SV-50A spectrometer. The temperature was controlled within 0.5° by circulating water at a constant temperature around the cell.

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