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H—D SCRAMBLING IN THE ETHYL GROUP(S) AND 2,2'-BIPYRIDINE LIGAND OF ETHYL-NICKEL, -IRON AND -COBALT COMPLEXES IN THEIR REACTIONS WITH MOLECULAR DEUTERIUM

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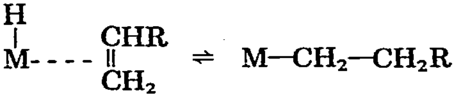
Summary

Reactions of $NiMe_2(bipy)$, (bipy = 2,2'-bipyridine), $NiEt_2(bipy)$, $FeEt_2(bipy)_2$, $CoMe(bipy)_2$, $CoEt(bipy)_2$, $NiEt(acac)(PPh_3)$ (acac = acetylacetonato, PPh_3 = triphenylphosphine), $CoMe(PPh_3)_3$, $CoEt_2(acac)(PPhMe_2)_2$, $CrMeCl_2(THF)_3$ and $RhMe(PPh_3)_3$ with molecular deuterium have been studied. Reactions of the methyltransition-metal complexes with D_2 gave only CH_3D and CH_4, whereas reactions of the ethyltransition-metal complexes with D_2 gave C_2D_6, C_2HD_5, $C_2H_2D_4$, $C_2H_3D_3$, and $C_2H_4D_2$ in addition to C_2H_5D and C_2H_6. A mechanism comprised of the oxidative addition of D_2, β-elimination and its reverse process, exchange of a hydrido with a deuterido ligand and reductive elimination of the deuterido and ethyl ligands, is proposed to account for the formation of the extensively deuterated ethanes. Hydrogen atoms of 2,2'-bipyridine ligand of the alkyltransition-metal complexes also undergo exchange with D_2, predominantly at the 4- and 6-positions.

Introduction

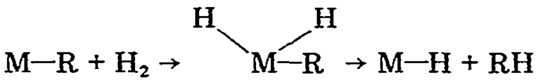
Insertion of an olefin into a transition-metal—hydrogen bond and its reverse process, β-elimination of an olefin from an alkyltransition-metal species, constitute the key steps in isomerization and hydrogenation reactions of olefins catalyzed by transition metals and their complexes [1] (eq. 1).



$$\overset{\displaystyle H}{\underset{}{\overset{|}{M}}}\text{- - - -}\begin{matrix}\text{CHR}\\ \|\\ \text{CH}_2\end{matrix} \rightleftharpoons M{-}CH_2{-}CH_2R \tag{1}$$

Evidence supporting that such a process involving olefin insertion and β-elimination is rapid on the NMR time scale has been presented recently [2]. When the reversible process occurs more slowly, it may not be observable by NMR spectroscopy but may be investigated by a chemical means employing labelled compounds. We recently have established that H—D scrambling was taking place in specifically deuterated ethyl-nickel and -cobalt complexes, $Ni(CH_2CD_3)(acac)(PPh_3)$ [3] and $Co(CH_2CD_3)_2(acac)(PPhMe_2)_2$ [4] (acac = acetylacetonato ligand) although the occurrence of the scrambling process in the ethylnickel complex on the NMR time scale was disproved [5].

The other important elementary processes in catalyzed reactions of olefins (such as hydrogenation and a chain transfer reaction in Ziegler type polymerization in the presence of molecular hydrogen) are the oxidative addition of dihydrogen forming a transition metal dihydride and the reductive elimination liberating an alkane. The latter process proceeds by coupling of an alkyl group with one of the hydrido ligands formed by the oxidative addition of H_2 [1] (eq. 2).



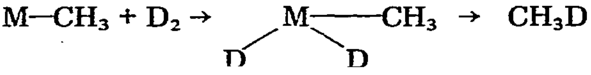
$$\mathrm{M{-}R + H_2 \rightarrow \overset{H\qquad H}{M{-}R} \rightarrow M{-}H + RH} \qquad (2)$$

There are limited examples dealing with the reaction of isolated alkyltransition-metal complexes with dihydrogen [6] and more information is desirable for understanding the crucial steps in the olefin catalyses. Employment of D_2 in its reaction with alkyltransition-metal complexes allows one to examine the deuterium-labelled alkanes produced by hydrogenolysis and thus provides a deeper insight into the reaction mechanism. Analysis of the isotopic distribution in the deuterium gas employed, after the reaction has been terminated, also affords supplementary information. In some cases deuterium is incorporated into other parts of the ligands attached to the transition metals. The extent and location of the H—D exchange reaction in the ligands may be confirmed by NMR spectroscopy. The present paper deals with the reaction of D_2 with various methyl- and ethyl-transition-metal complexes with tertiary phosphines and 2,2′-bipyridine ligands and discusses the mechanisms of the hydrogenolysis of such transition-metal complexes.

Results and discussion

Reaction of methyltransition-metal complexes with D_2

All of the methyltransition-metal complexes employed, including $CoMe(PPh_3)_3$ (PPh_3 = triphenylphosphine), $CoMe(bipy)_2$ (bipy = 2,2′-bipyridine), $NiMe_2(bipy)$, $CrMeCl_2(THF)_3$ and $RhMe(PPh_3)_3$, liberated CH_4 and CH_3D by the reactions with D_2 in toluene (Table 1). $CoMe(PPh_3)_3$, $CoMe(bipy)_2$ and $RhMe(PPh_3)_3$ were degraded completely during the reaction. In contrast, $NiMe_2(bipy)$ and $CrMeCl_2(THF)_3$ were more stable and considerable part of the complexes remained unchanged. CH_4 may be formed by thermolysis of the methyltransition-metal complexes in the solvent and CH_3D by the reaction of D_2, presumably through the process shown in eq. 3.



$$\mathrm{M{-}CH_3 + D_2 \rightarrow \underset{D\qquad D}{M{-}CH_3} \rightarrow CH_3D} \qquad (3)$$

TABLE 1

REACTIONS OF THE METHYLTRANSITION-METAL COMPLEXES WITH D_2 IN TOLUENE

No.	Complex (mmol)	D_2 (mmol)	Temperature (°C)	Time	$CH_3D/(CH_3D + CH_4)$
1	$CoMe(PPh_3)_3$ (0.52)	18	25	1 day	0.42
2	$CoMe(PPh_3)_3$ (0.35)	18	0	1 day	0.89
3	$CoMe(bipy)_2$ (0.60)	14	75	12 h	0.10
4	$NiMe_2(bipy)$ (0.61)	10	r.t.	1 day	0.53
5	$CrMeCl_2(THF)_3$ (1.2)	10	r.t.	1 day	0.07
6	$RhMe(PPh_3)_3$ (0.44)	18	25	1 day	1.0

Extensively deuterated methanes, CH_2D_2, CHD_3, and CD_4, were not formed in the reactions of the methyltransition-metal complexes with D_2, the fact suggesting that the formation of a carbenoid species by α-elimination from the methyl group did not take place during the reaction *.

Reactions of ethyltransition-metal complexes with D_2

In the reactions with D_2 the ethyltransition-metal complexes, $NiEt_2(bipy)$, $CoEt(bipy)_2$, $FeEt_2(bipy)_2$, $NiEt(acac)(PPh_3)$, and $CoEt_2(acac)(PPhMe_2)_2$ (acac = acetylacetonato ligand), liberated polydeuterated ethanes in addition to C_2H_5D. The latter is expected to be the sole deuterated product formed by simple cleavage of the ethyl—nickel bond by D_2 according to eq. 2. Table 2 shows the distribution of the deuterated and non-deuterated ethanes evolved in the reactions of the ethyltransition-metal complexes with D_2 in toluene. Non-deuterated ethane, C_2H_6, may have been formed, at least partly, by thermolysis of the complexes in solution.

$NiEt_2(bipy)$ liberated 16 mol % of ethane per nickel on reaction with D_2 for 50 h at 45°C. The mass spectrum of the ethane evolved showed the existence of variously deuterated ethanes ranging from -d_6 to -d_0 as shown in Table 2. Since $NiEt_2(bipy)$ does not catalyze the H—D exchange reaction between ethane and D_2 (see Experimental), ethanes from -d_6 to -d_2 are considered to be formed as a result of H—D scrambling of the ethyl groups and their deuterolysis.

The precise mechanism of the H—D scrambling of the ethyl groups on reaction with D_2 is not known on the basis of presently available techniques. The ethyl groups may liberate deuterated ethanes on their direct interaction with D_2 or through intermediate, unstable, oxidative addition products of $NiEt_2(bipy)$ with D_2 followed by subsequent β-elimination and reinsertion processes, and reductive elimination of the ethyl and deuterido ligands (Scheme 1).

In Scheme 1 the deuteration of the ethyl ligand is postulated to proceed through the conventional β-elimination and reinsertion processes. As another conceivable elementary step rotation of ethylene ligand in III around the axis connecting nickel and the center of the coordinated ethylene may be involved. However, it is omitted in the scheme for clarity. In Scheme 1 the intermediacy

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* The formation of CD_4, CHD_3 and CH_2D_2 in addition to CH_3D and CH_4 in the reactions of $CoMe(PPh_3)_3$ and $RhMe(PPh_3)_3$ with D_2 in toluene was reported [6e]. However, the conclusion drawn in the paper was based on misinterpretation of the mass spectral data and corrected later [26].

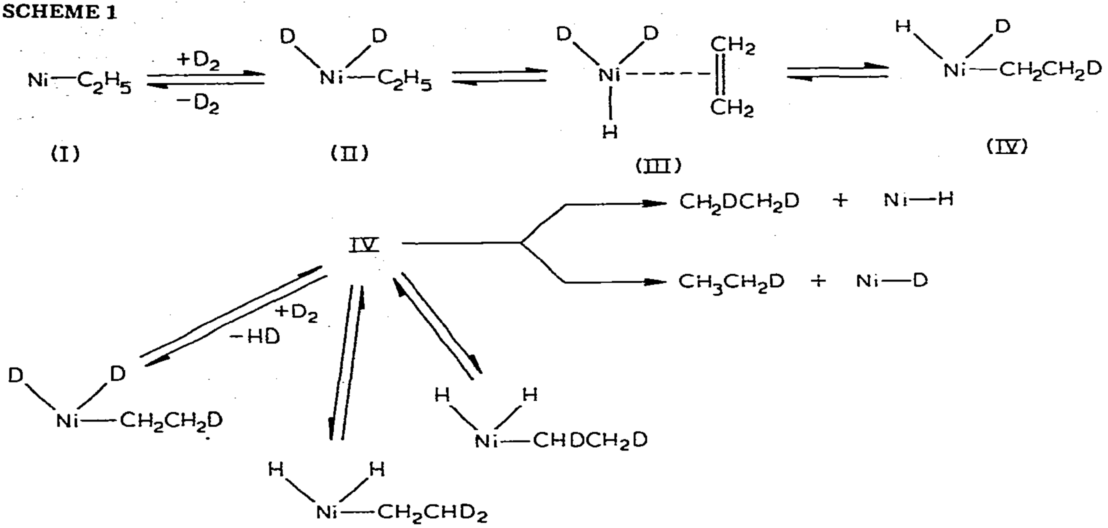
TABLE 2

THE DISTRIBUTION OF DEUTERATED AND NON-DEUTERATED ETHANES FORMED BY THE REACTIONS OF THE ETHYLTRANSITION-METAL COMPLEXES WITH D_2 IN TOLUENE

No.	Complex (mmol)	D_2 (mmol)	Temperature (°C)	Time (h)	Ethane/ metal [a]	D_2 [b] purity	Distribution of ethanes							
							-d_6	-d_5	-d_4	-d_3	-d_2	-d_1	-d_0	M [c]
1	$NiEt_2(bipy)$ (1.3)	15.0	45	50	0.16	0.91	0.2	0.7	0.7	3.9	15	42	37	1.45
2	$NiEt_2(bipy)$ (0.70)	6.0	65 ± 5	20	0.06	0.72	0.6	1.0	1.8	4.0	24	37	32	1.66
3	$FeEt_2(bipy)_2$ (0.51)	10.0	65 ± 5	10	1.32	0.81	3.0	3.4	2.4	2.8	4.3	64	20	1.57
4	$CoEt(bipy)_2$ (1.20)	16.0	75 ± 5	2	0.41	0.78	0	1.5	3.6	4.6	15	13	62	2.07
5	$NiEt(acac)(PPh_3)$ (0.75)	2.1	18	72	0.04	0.96	9	12	15	18	46	trace	trace	3.20
6	$NiEt(acac)(PPh_3)$ (0.47)	15.0	25	72	—	—	4	9	15	22	49	trace	trace	2.93
7	$CoEt_2(acac)(PPhMe_2)_2$ (0.20)	7.4	5	8	0.30	—	0	0	0	0	trace	5.5	94	1.00
8	$CoEt_2(acac)(PPhMe_2)_2$ (0.15)	1.9	40	6	0.62	—	0	0	0.3	1.1	2.1	8.3	88	1.42

[a] Moles of the ethane formed per mole of the complex. [b] Isotopic purity of the deuterium gas recovered after the reaction. [c] Multiple exchange parameter [25].

SCHEME 1



of a tetravalent nickel complex is assumed as the oxidative addition product of D_2 to the diethylnickel(II) complex. Although no stable nickel(IV) complex has been reported, the precedents of the corresponding organoplatinum(IV) complexes [7] do not make the postulate of the intermediate, unstable, dihydridodiethylnickel(IV) complex entirely irrelevant.

The ethylcobalt and diethyliron complexes coordinated with two bipy ligands also underwent H—D scrambling reactions, liberating extensively deuterated ethanes in addition to ethane-d_1 and -d_0. In contrast to the four coordinate diethylnickel complex which has a vacant site to interact with a D_2 molecule, these ethyl-iron and -cobalt complexes with two bipy ligands may not have the available vacant site. Hence a partial dissociation of the bipy ligands may be required in order to provide a vacant site for interaction with D_2, as we have assumed, based on kinetic results in the polymerization of olefins with the dialkylbis(2,2'-bipyridine)iron(II) complexes [8]. The reaction of D_2 with another diethylnickel(II) complex, $NiEt_2(dpe)$ (dpe = 1,2-bis(diphenylphosphino)-ethane), gave only the thermolysis products, C_2H_6 and C_4H_{10} in a molar ratio of 1 : 10.

Mass spectroscopic examination of the deuterium gas after the reaction with the bipy-coordinated ethyl-nickel, -cobalt and -iron complexes showed a decrease of the D_2 content and an increase of the HD and H_2 contents. The ratios between D_2, HD and H_2 were statistical, in agreement with the assumption of random mixing.

Despite the formation of polydeuterated ethanes on reaction of D_2 with $NiEt_2$(bipy), examination of the remaining complex after treatment with D_2 revealed that it contained no deuterium in the nickel-bonded ethyl groups as proved by NMR analysis of the complex recovered from the solution and also by a mass spectroscopic examination of the ethane formed on acidolysis of the recovered complex with H_2SO_4.

These results suggest that the H—D scrambling takes place only when the bipy-coordinated ethyl complexes undergo hydrogenolysis and the remaining ethyl complexes are kept intact.

We have separately observed that $Co(CH_2CD_3)_2(acac)(PPhMe_2)_2$ undergoes H—D scrambling only in the process of thermolysis [4] as in the thermolysis of a deuterated ethylplatinum complex [9], whereas H—D scrambling in the ethyl group of $Ni(CH_2CD_3)(acac)(PPh_3)$ takes place slowly without appreciable decomposition of the complex [3]. Examination of the interactions of D_2 with $NiEt(acac)(PPh_3)$ and $CoEt_2(acac)(PPhMe_2)_2$ revealed the difference in behavior of these ethyl-nickel and -cobalt complexes. $NiEt(acac)(PPh_3)$ behaves quite differently from the bipy-coordinated ethyl complexes toward D_2. As shown in Table 2, the ethane evolved contained only negligible amounts of ethane-d_1 and ethane-d_0 and quite significant fractions of polydeuterated ethane-d_2 to -d_6. Examination of the remaining ethyl(acetylacetonato)nickel complex after treatment with D_2 revealed again that no deuterium was incorporated into the remaining ethylnickel complex.

On the other hand, deuterium introduction into the ethane produced in the reaction of D_2 with $CoEt_2(acac)(PPhMe_2)_2$ was much less pronounced (Table 2). Our previous observation using $Co(CH_2CD_3)_2(acac)(PPhMe_2)_2$ indicated that a slow decomposition below 5°C gives clean β-elimination products, $CH_2{=}CD_2$ and CH_2DCD_3, whereas thermolysis in solution at 50°C in benzene liberated some H—D scrambling products. In the present study the reaction of $CoEt_2$-$(acac)(PPhMe_2)_2$ with D_2 at 5°C liberated non-deuterated ethylene and ethane in 1/1 ratio, whereas the similar reaction at 40°C released slightly deuterated ethanes and ethylenes in ca. 2 : 1 ratio. These results reveal the pronounced tendency of the nickel-bonded ethyl group in $NiEt(acac)(PPh_3)$ toward scrambling.

The differences in the distributions of the deuterated ethanes produced by D_2 interaction with the ethyltransition-metal complexes may be accounted for by assuming a rate difference in each elementary step in Scheme 1, such as (a) the oxidative addition of D_2, (b) β-elimination and reinsertion of ethylene, (c) the reductive elimination of the ethyl and hydrido or deuterido ligands to liberate ethane, (d) the exchange of the hydrido with the deuterido ligands, and (e) the reductive elimination of the hydrido and deuterido ligands producing H_2, HD and D_2. If the reductive elimination of the ethyl and the hydrido ligands (step c) is slower than the other elementary steps (a,b,d,e), the formation of ethanes more extensively deuterated than ethane-d_2, as observed in the reaction of D_2 with $NiEt(acac)(PPh_3)$, may be accounted for.

The IR spectroscopic examination of the ethane gas evolved in the reaction of $NiEt(acac)(PPh_3)$ with D_2 demonstrated that it contained mainly 1,2-polydeuterated ethanes contaminated with trace amounts of ethanes having CH_3 group(s) (CH_3CH_3, CH_3CH_2D, CH_3CHD_2 and CH_3CD_3). This IR spectroscopic observation not only gives additional support for the absence of ethane-d_0 and -d_1, the conclusion arising from the mass spectral analysis of the gas, but is consistent with the assumption that the H—D exchange in the hydrido ligand(s) with the gas phase D_2 takes place rapidly prior to reductive elimination of the hydrido and ethyl-d_n ligands. The PPh_3 ligand in $NiEt(acac)(PPh_3)$ was found not to be deuterated in the reaction with D_2 as proved by the mass spectrometric examination of the PPh_3 ligand liberated on acidolysis of the recovered ethylnickel complex with D_2SO_4.

These results suggest that interaction of D_2 with the ethyltransition-metal complexes, presumably through oxidative addition of D_2 to the complexes, may lead to activation of the metal—ethyl bond, thus making it susceptible to β-elimination and reinsertion processes represented by Scheme 1.

The assumption of direct interaction of D_2 with the metal-bonded ethyl group, a process proceeding without involvement of the oxidative addition of D_2, seems less probable, since such a process would give deuterated ethyltransition-metal complexes which would liberate deuterated ethanes on acidolysis.

Deuteration of the 2,2'-bipyridine ligand

The 2,2'-bipyridine ligands in $NiEt_2(bipy)$, $FeEt_2(bipy)_2$, $CoEt(bipy)_2$, and Ni(bipy)(man) (man = methacrylonitrile) exchanged their hydrogens with D_2. Table 3 summarizes the results. The NMR spectrum (Fig. 1) of bipy obtained by acidolysis of $NiEt_2(bipy)$ recovered after the reaction with D_2 (No. 1 in Table 2) shows a very drastic decrease of 4-H and 6-H signals compared with those of normal bipy. Both the doublet of 3-H and the triplet of 5-H in bipy became singlets due to the extensive deuteration of the 4- and 6-positions.

The IR spectrum (Fig. 2) of 2,2'-bipyridine which was obtained by acidolysis of $NiEt_2(bipy)$ after its contact with D_2 shows ν(CD)s at 2250 and 2270 cm^{-1} as well as isolated out-of-plane vibration (δ(CH)) at 915 cm^{-1}, the isolated δ(CD) at 650 cm^{-1} ($\delta(CH)/\delta(CD) = 1.41$) and other new out-of-plane vibrations in the region from 600 to 900 cm^{-1}. The mass spectrum of bipy recovered cuts off at *m/e* 163 corresponding to the $[^{12}C_9{}^{13}C_1{}^{1}H_2{}^{2}H_6{}^{14}N_2]^+$ parent ion. Since the H—D exchange in the bipy ligand took place even in $NiEt_2(bipy)$ whose ethyl groups did not undergo H—D exchange, the H—D exchange in the bipy ligand is considered to proceed independently of the H—D exchange in the ethyl groups.

The bipy ligands in $FeEt_2(bipy)_2$ and $CoEt(bipy)_2$ also underwent H—D exchange reactions with D_2, predominantly at the 4- and 6-positions.

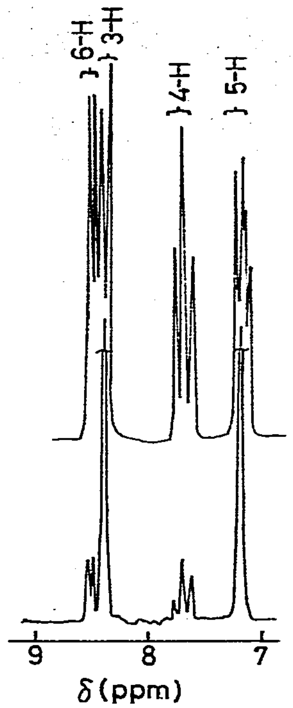
Among complexes of type $M(bipy)_m(olefin)_n$, the complex with a less electron-withdrawing olefin, Ni(bipy)(methacrylonitrile), underwent H—D exchange, but complexes with a more electron-withdrawing olefin, $Ni(bipy)(maleic\ anhydride)_2$ and $Fe(bipy)(maleic\ anhydride)_4$, did not. Free bipy, Li^+bipy^-, and transition-metal-bipy complexes with Cl or CN ligands, ($NiCl_2(bipy)$ and $FeX_2(bipy)_2$ (X = Cl, CN)), did not undergo H—D exchange at 60°C, either.

TABLE 3

THE DEUTERATION OF 2,2'-BIPYRIDINE LIGAND OF ORGANOTRANSITION-METAL COMPLEXES BY THE REACTION WITH D_2 IN TOLUENE

No.	Complex (mmol)	D_2 (mmol)	Temperature (°C)	Time (h)	Degree of deuteration (%) position of bipy				D_2 purity
					3	4	5	6	
1	$NiEt_2(bipy)$ (1.3)	15.0	45	50	10	90	25	55	91
2	$NiEt_2(bipy)$ (0.70)	6.0	65 ± 5	20	10	80	15	76	72
3	$FeEt_2(bipy)_2$ (0.51)	10.0	65 ± 5	10	—	79	29	84	81
4	$CoEt(bipy)_2$ (1.20)	16.0	75 ± 5	2	—	90	0	75	78
5	Ni(bipy)(man) [a] (1.70)	9.3	75 ± 5	12	—	10	0	40	86

[a] man = methacrylonitrile.



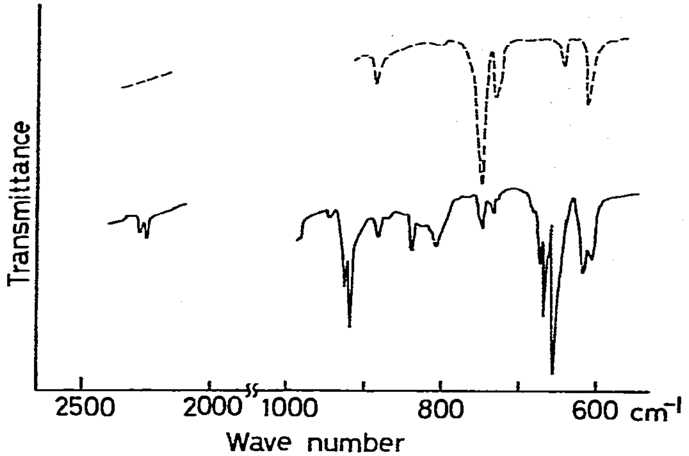


Fig. 1. Lower spectrum: NMR spectrum of 2,2′-bipyridine obtained by the acidolysis of the recovered diethyl(2,2′-bipyridine)nickel after the reaction with D_2 (No 1 in Table 3); solvent CCl_4. Upper spectrum: NMR spectrum of normal bipy. Chemical shift is referred to internal TMS (down-field positive).

Fig. 2. IR spectrum of 2,2′-bipyridine obtained by the acidolysis of recovered diethyl(2,2′-bipyridine)-nickel. Broken line shows the IR spectrum of normal bipy.

The H—D exchange of hydrogens in alkali metal salts of aromatic hydrocarbons with D_2 [10] and that in ligands (such as PPh_3 [11], triphenyl phosphite [11] and π-cyclopentadienyl [12], etc.) of transition-metal complexes have been reported. Recently deuteration of hydrocarbons catalyzed by transition-metal compounds in a solution of acidic deuterium oxide was also reported [13].

The *ortho*-metallation of PPh_3 and $P(OPh)_3$ ligands and the successive cleavages of the metal—carbon bonds by D_2 are widely accepted as elementary steps in the deuteration of the tertiary phosphine and phosphite ligands [11].

A similar assumption of the intramolecular metallation mechanism in the present system would entail the supposition of an extremely strained, unplausible intermediate. However, the possibility of an intermolecular metallation mechanism may not be excluded.

Another possible mechanism is a direct replacement of hydrogens in the bipy ligand by deuterido ligands, a process without internal metallation of the bipy ligand. The deuterido ligand may approach the bipy ligand in a certain activation state through an intermolecular process and may replace the hydrogens of bipy by deuteriums.

The fact that the H—D exchange reaction occurs predominantly at the 4- and

6-positions of bipy ligand in the complexes which are essentially in the low oxidation state [14], whereas it does not occur in complexes having strongly electronegative ligand, suggests an electrophilic substitution mechanism for the H—D exchange reaction and the importance of the $p\pi$—$d\pi$ interaction between the central transition metal and the bipy ligand.

Experimental

Reagents

Molecular deuterium was used as purchased from Showa Denko Co. Ltd. The isotopic purity of the D_2 gas employed was about 99.5%. Toleune was purified and dried by the usual procedures and stored under nitrogen. $NiEt_2$(bipy) [14, 15], $NiMe_2$(bipy) [14], $FeEt_2(bipy)_2$ [8,15a,b], $CoEt(bipy)_2$ [16], NiEt(acac)-(PPh_3) [3], $Ni(bipy)(olefin)_n$ [14], $NiCl_2$(bipy) [14], Fe(bipy)(maleic anhydride)$_4$ [8], $CoMe(bipy)_2$ [16], $CrMeCl_2(THF)_3$ [17], $CoEt_2(acac)(PPhMe_2)_2$ [4], and $CoMe(PPh_3)_3$ [18] were prepared as previously reported. $RhMe(PPh_3)_3$ was prepared by Keim's method [19]. $FeCl_2(bipy)_2$ and $Fe(CN)_2(bipy)_2$ [20] were kindly offered by Dr. T. Saji of our Institute.

Reaction of transition-metal complexes with D_2 and the analyses of the gases evolved

A typical experimental procedure for the exchange reactions is as follows. Toluene (10 ml) was distilled into a Schlenk type flask containing 0.35 g (1.3 mmol) of $NiEt_2$(bipy) by trap-to-trap distillation in vacuum. D_2 (340 ml, STP, 15 mmol) was introduced into the reaction vessel and the solution was stirred at 45°C. After 50 h 0.21 mmol of ethane was collected as measured by volumetry after removal of D_2 by pumping from the condensed ethane at liquid nitrogen temperature. The ethane thus collected was subjected to mass spectroscopic analysis. Butane, the thermolysis product of $NiEt_2$(bipy) [14,15], was evolved in the reaction. However, the amount was negligible compared with the amount of ethane. The other reactions of methyl- and ethyl-transition-metal complexes with D_2 were carried out in analogous manners. The amount of methane involved in the reactions of the methyltransition-metal complexes with D_2 was not measured due to the difficulty of separating methane from D_2 quantitatively. Methane employed for mass spectroscopy was freed from D_2 by a fractional adsorption method on active charcoal powder at —196°C in order to avoid possible emergence of false peaks in the mass spectrum. The isotopic purity of molecular deuterium after the reaction and the composition of the deuterated and non-deuterated alkanes in the gas evolved were determined by mass spectrometry with a Hitachi mass spectrometer model RMU-5B. The fragmentation pattern of each deuterated methane [21] and ethane [22] is given in the literature. 2,2'-Bipyridine was liberated from the reaction system by acidolysis of the recovered $NiEt_2$(bipy) or the reaction residue followed by extraction with diethyl ether and recrystallization from hexane.

NMR and IR spectral measurement

NMR spectra of recovered $NiEt_2$(bipy) and bipy were measured by Mr. Y. Nakamura of our Research Laboratory with a Japan Electron Optics Laboratory

PS-100 spectrometer. Assignment of each signal of the complex [23] and ligand [24] is given in the literature. The average degree of deuteration of bipy ligand in $NiEt_2$(bipy) was calculated by comparing the sum of areas of bipy signals with that of ethyl signals in the NMR spectrum of the recovered $NiEt_2$(bipy), whose ethyl signals showed no deuterium introduction into the ethyl group. The 3-H signals and 4-H signals of bipy ligand in the complex were not separated. The relative intensity of the signal of each hydrogen of bipy was calculated from the NMR spectrum of bipy (Fig. 1). Thus the degree of deuteration at each position of the bipy ligand in $NiEt_2$(bipy) was obtained. The degree of deuteration of the bipy ligand in the complexes other than $NiEt_2$(bipy) was calculated from the NMR spectrum of bipy obtained by acidolysis of the reaction residue, since these complexes were either difficult to recover from the reaction system or gave only broadened obscure NMR peaks presumably due to paramagnetic species formed in the reaction. In these cases the strongest NMR peak of the recovered bipy, i.e., the 3-H peak, was referred to as the standard by assuming a negligible deuterium introduction into the 3-position.

IR spectra were measured by using a Hitachi Model EPI-G3 spectrometer. The IR spectra of the ethane gases evolved by the reactions of ethyltransition-metal complexes with D_2 generally showed three strong bands at 2950 (ν(CH)), 2200 (ν(CD)) and 1450 cm^{-1} ($\delta(CH_3)$). However, the absorption band at 1450 cm^{-1} for the ethane gas evolved by the reaction of NiEt(acac)(PPh_3) with D_2 was very weak, indicating the presence of only trace amounts of C_2H_6, C_2H_5D, 1,1-ethane-d_2 and 1,1,1-ethane-d_3 in the ethane gas.

Reaction of C_2H_6 with D_2 in the presence of $NiEt_2$(bipy)

A mixture of normal ethane (23 ml) and D_2 (210 ml) was allowed to react at 45°C for 23 h in the presence of 10 ml of a toluene solution containing $NiEt_2$(bipy) (100 mg, 0.4 mmol). The mass spectrum of ethane after the reaction showed the presence of only negligible amounts of deuterated ethanes which are considered to be formed by the reaction of $NiEt_2$(bipy) with D_2.

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