Chem. Ber. **119**, 2531–2541 (1986)

Reductive Elimination from (2,2′-Bipyridine)diethylpalladium(II), a Mechanistic Study

*Reiner Sustmann** and *Jürgen Lau*

Institut für Organische Chemie der Universität Essen,
D-4300 Essen 1, Postfach 103764

Received February 24, 1986

(2,2′-Bipyridine)diethylpalladium(II) (1) is synthesized and its thermolysis in the presence and absence of additives is studied. Thermolysis, neat or in solution, yields ethane and ethene as products. Addition of methyl acrylate reverses the product composition completely to *n*-butane. Kinetic measurements as function of additives, 2,2′-bipyridine or methyl acrylate, demonstrate that disproportionation products are formed by a dissociative and a nondissociative pathway. Methyl acrylate enters the rate limiting step of *n*-butane formation.

Reduktive Eliminierung aus (2,2′-Bipyridin)diethylpalladium(II), eine mechanistische Studie

Die Synthese von (2,2′-Bipyridin)diethylpalladium(II) (1) und seine Thermolyse in Gegenwart und in Abwesenheit von Additiven wird beschrieben. Feststoffthermolyse oder Zersetzung in Lösung ergibt Ethan und Ethen, während Thermolyse in Diphenylmethan in Gegenwart von Methylacrylat vollständige Produktumsteuerung zu *n*-Butan bewirkt. Kinetische Messungen als Funktion zugesetzten 2,2′-Bipyridins und Methylacrylats zeigen, daß die Disproportionierungsprodukte auf einem dissoziativen und einem nichtdissoziativen Weg gebildet werden. Methylacrylat ist am geschwindigkeitsbestimmenden Schritt der *n*-Butanbildung beteiligt.

Reductive eliminations from diorganyl-d^8-transition metal complexes with formation of a new carbon-carbon bond are important steps in stoichiometric and catalytic processes. CC bond formation can be achieved if the organic ligands are phenyl[1], allyl[2,3], alkenyl[4], or alkyl groups without β-hydrogen atoms[5–8]. If saturated aliphatic groups with β-hydrogen atoms are involved complications in CC bond forming reactions may arise. In competition to reductive elimination β-hydrogen transfer and formation of disproportionation products may then take place[9,10]. In the majority of cases the latter process dominates the reaction rendering such dialkyl-d^8-transition metal complexes useless as intermediates in synthetic sequences.

Yamamoto[11] described that (2,2′-bipyridine)diethylnickel(II)[12,13] forms *n*-butane on thermolysis either neat or in the presence of added olefin. He also showed in a study with diethylbis(tert. alkylphosphane)palladium(II) complexes that a *cis*-arrangement of the alkyl ligands in these square planar complexes is a necessary prerequisite for CC bond formation[7,14]. So far no other examples of dialkyl-d^8-transition metal complexes with β-hydrogen atoms in the ligands were reported in which reductive elimination is observed. Recently we found[15] that (2,2′-bipyridine)diethylpalladium(II) yields disproportionation products on thermolysis, neat or in solution, however gives almost quantitatively *n*-butane if electron deficient olefins are added.

0009–2940/86/0808–2531 $ 02.50/0

In this communication kinetic studies have been carried out in order to gain insight in the mechanism of this reaction. The decomposition of the complex was studied as a function of added 2,2′-bipyridine, as a function of added olefin, and by studying the combined effect of olefin and 2,2′-bipyridine.

Results

(2,2′-Bipyridine)diethylpalladium(II) (**1**) was prepared by the reaction of (acetylacetonato)palladium with diethylaluminum ethoxide in the presence of 2,2′-bipyridine similar to the preparation of (2,2′-bipyridine)diethylnickel(II)[12,13].

$$Pd(acac)_2 + Al(OC_2H_5)(C_2H_5)_2 + bpy \longrightarrow (C_2H_5)_2Pd(bpy) + Al(OC_2H_5)(acac)_2$$

1

Thermolysis of complex **1** was carried out on a high vacuum line. The amount of liberated gaseous products was determined with a Toepler pump, the composition of the gas was obtained by GLC. After 30 minutes at 110°C without solvent the gaseous products, formed in almost quantitative yield, were as shown in Table 1. Besides traces of butane the main products are ethane and ethene. In addition metallic palladium and 2,2′-bipyridine can be identified. The composition of the gas remains unchanged if the reaction is carried out in diphenylmethane as solvent at 80°C for four hours. During this time the solution becomes almost colourless while metallic palladium deposits.

Table 1. Products formed in thermolysis of (2,2′-bipyridine)diethylpalladium(II) (**1**) (R_{-H} = ethyl − H for $H_2C{=}CH_2$)

Complex	Solvent	Additive bpy[b]	Additive Ma[c] (equiv.)	T °C	t h	R_{-H} %	RH %	R−R %	Yield[a] %
$(C_2H_5)_2Pd(bpy)$	–	–	–	110	0.5	44	51	3	94
$(C_2H_5)_2Pd(bpy)$	Ph_2CH_2	–	–	80	4.0	45	53	2	70
$(C_2H_5)Pd(bpy)$	C_6H_6	10	–	80	5.0	45	45	1	61
$(C_2H_5)_2Pd(bpy)$	Ph_2CH_2	–	10	25	20	8	3	89	100

[a] Yield = $(0.5\,R_{-H} + 0.5\,RH + R{-}R)\cdot 100/(\text{complex})$, error ±5%. – [b] 2,2′-Bipyridine. – [c] Methyl acrylate.

A kinetic study was initiated to provide information about the mechanism of decomposition of **1**. At 80°C ^1H NMR signals of the ligands 2,2′-bipyridine and ethyl were followed for at least 2.5 half lifes. Measurements were performed as a function of added 2,2′-bipyridine. The decomposition follows a first order rate law, the rate constants are collected in Table 2. Fig. 1 displays graphically the rate constants as function of 2,2′-bipyridine concentration.

Table 2. Dependence of the first order rate constant for the thermolysis of $(C_2H_5)_2Pd(bpy)$ (**1**) as a function of added 2,2'-bipyridine at 80 ± 2.5°C

No.	2,2'-Bipyridine mol/l	k min^{-1}	$\frac{\text{2,2'-Bipyridine}}{(C_2H_5)_2Pd(bpy)}$[a]
1	0.000	0.0250 ± 0.0002	0
2	0.078	0.0127 ± 0.0002	0.78
3	0.145	0.0101 ± 0.0003	1.45
4	0.260	0.0065 ± 0.0001	2.60
5	0.500	0.0054 ± 0.0002	5.00
6	0.660	0.0050 ± 0.0001	6.60
7	1.000	0.0039 ± 0.0001	10.00
8	1.420	0.0055 ± 0.0003	14.00
9	1.780	0.0052 ± 0.0001	17.80

[a] Concentration of $(C_2H_5)_2Pd(bpy)$ = 0.100 mol/l in [D_7]DMF.

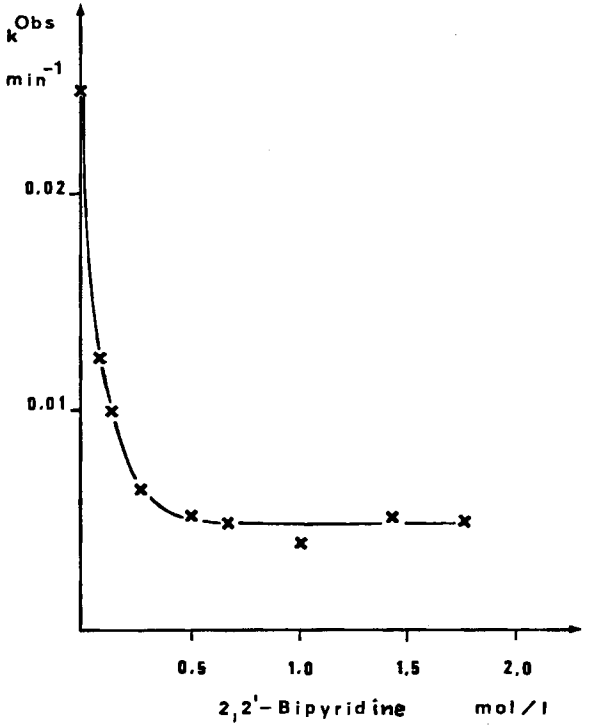


Fig. 1. First order rate constant for the thermolysis of $(C_2H_5)_2Pd(bpy)$ (**1**) as a function of added 2,2'-bipyridine

A decrease in the rate constant is noticed which approaches a limiting value at a fivefold excess of 2,2'-bipyridine. A product analysis at a tenfold excess of 2,2'-bipyridine ascertained (see Table 1) that no change in product composition had occurred.

The complete change to butane as product of a reductive elimination if methyl acrylate is added (see Table 1) prompted rate measurements in order establish the order of this process. In Fig. 2 UV spectra are shown which were recorded during the decomposition of **1** in the presence of methyl acrylate. The rate constants were determined from the change in extinction at 496 nm even though an unstable, not isolable reaction product shows absorption at this wave length.

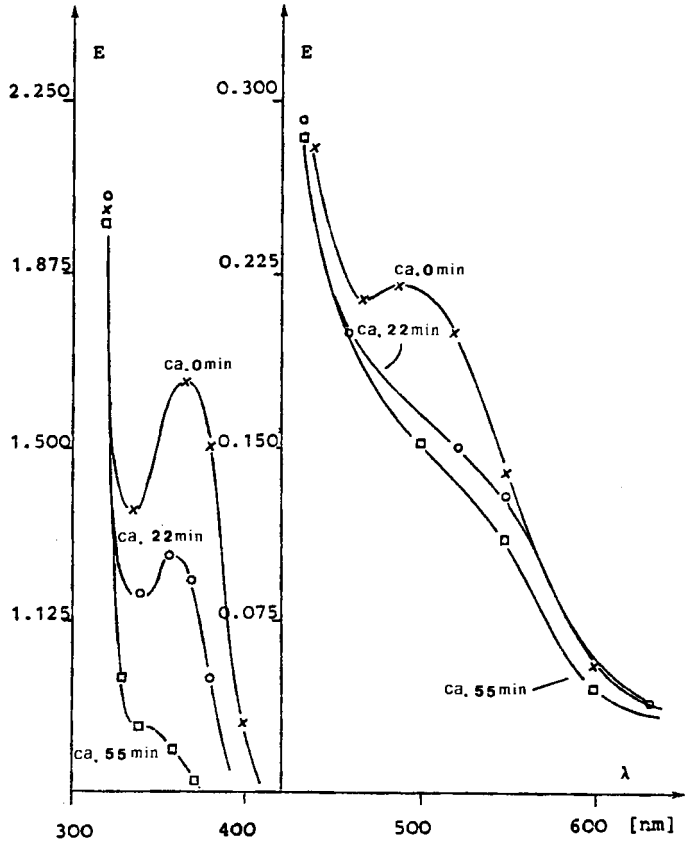


Fig. 2. UV spectra during the reaction of $(C_2H_5)_2Pd(bpy)$ (**1**) (0.0015 M) with methyl acrylate (0.015 M in THF)

Table 3 lists rate constants at 22°C for increasing fractions of methyl acrylate (367–1833 fold excess). The high concentration of methyl acrylate was chosen in order to avoid complications which arise at long reaction times due to deposition of metallic palladium.

A plot of k vs. concentration of methyl acrylate leads to a second order rate constant for the overall reaction of $0.97 \times 10^{-3} l mol^{-1} s^{-1}$ at 22°C in tetrahydrofuran.

An attempt was made to recognize an intermediate in the reaction of **1** with methyl acrylate by ^1H NMR spectroscopy. *Yamamoto* in his studies on (2,2'-

Table 3. Pseudo first order rate constants for the reactions of $(C_2H_5)_2Pd(bpy)$ (**1**) with increasing methyl acrylate concentration in tetrahydrofuran at 22°C

No.	Methyl acrylate mol/l	$\frac{\text{Methyl acrylate}}{(C_2H_5)_2Pd(bpy)}$[a]	k s^{-1}
1	0.55	367	0.00117
2	1.10	733	0.00227
3	1.65	1100	0.00214
4	2.20	1466	0.00325
5	2.75	1833	0.00335

[a] Concentration of $(C_2H_5)_2Pd(bpy)$ = 0.0015 M.

Table 4. Gaseous products in the reaction of $(C_2H_5)_2Pd(bpy)$ (**1**) with methyl acrylate and 2,2′-bipyridine in the molar ratio 1:10:10 at 25°C in diphenylmethane (total yield after 1160 min: 58%)

No.	t min	Ethene %	Ethane %	Butane %	Pressure Torr
1	0	–	–	–	3
2	10	14.7	11.3	71.7	8
3	25	12.0	24.5	60.7	10
4	40	9.1	34.6	34.0	11
5	55	6.9	43.7	47.7	12
6	70	5.1	49.8	43.1	13
7	85	4.0	56.2	38.0	14
8	100	3.2	59.6	35.2	15
9	115	2.7	62.5	32.9	16
10	130	2.4	63.9	31.6	16.5
11	180	2.1	65.6	30.5	17
12	1160	2.4	72.4	23.5	19.5

bipyridine)diethylnickel(II) detected at −70°C a change in the chemical shift of the ethyl protons if he added acrolein[16]. This was interpreted in terms of an association of acrolein with (2,2′-bipyridine)diethylnickel(II). Isolation of this complex was not possible because of reductive elimination of butane at higher temperatures (0°C). If **1** and a fivefold excess of methyl acrylate are dissolved in [D_7]DMF the ^1H NMR spectrum does not show changes in the proton signals of **1**. Fig. 3 represents spectra immediately after warming the reaction mixture from −50 to +22°C, after 2 hours and after 72 hours at room temperature. After 72 h most of the complex **1** has disappeared and signals of butane and also ethene are formed. Also 2,2′-bipyridine is no longer coordinated. The line broadening of the signals of the vinylic protons during the reaction is indicative of an interaction of methyl acrylate with **1**. Immediately after mixing and after termination of the reductive elimination these signals are sharp. The line broadening is taken as evidence of a reversible association of methyl acrylate with complex **1**.

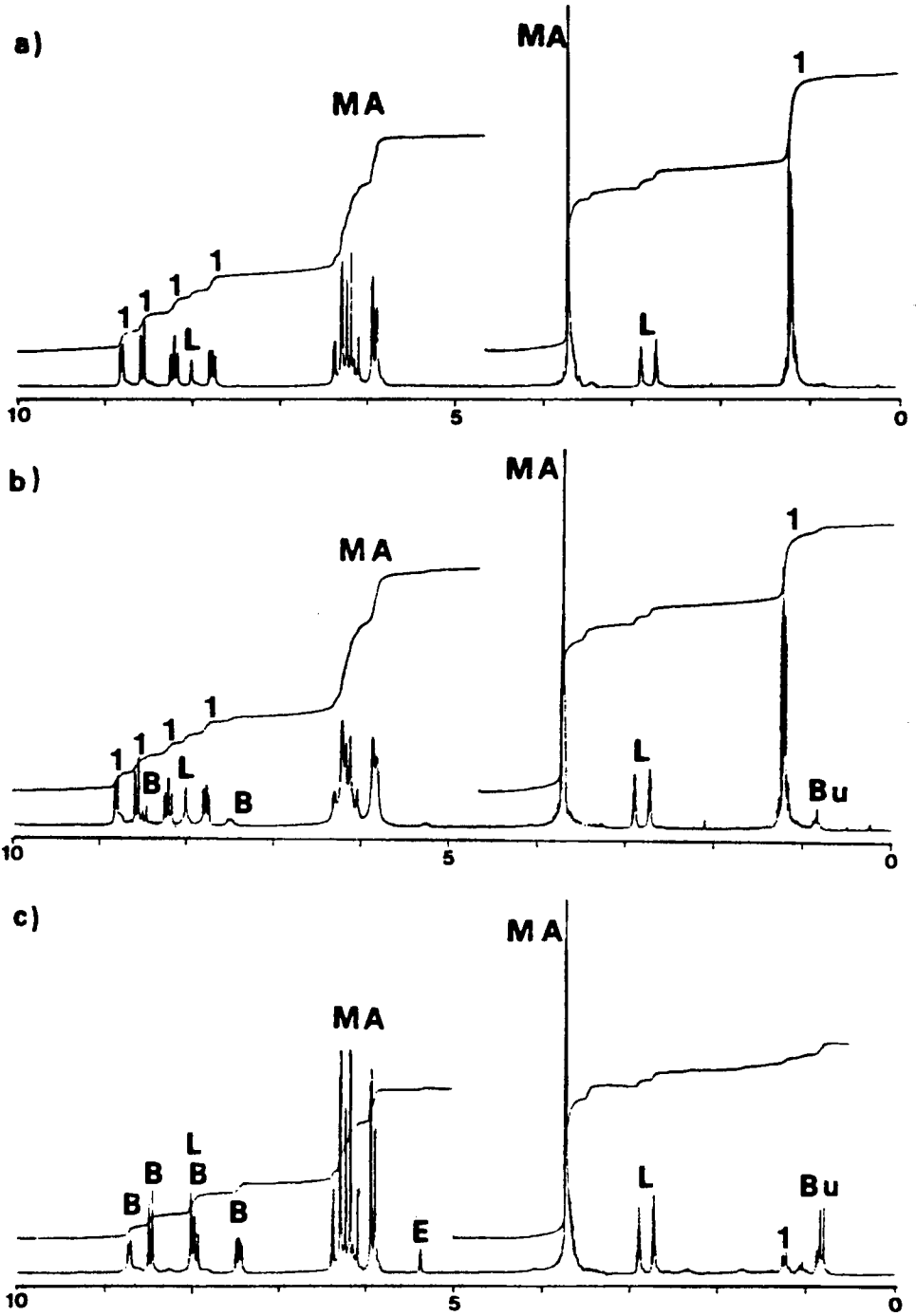


Fig. 3. ^{1}H NMR spectra during the reaction of $(C_2H_5)_2Pd(bpy)$ (1) with five equivalents of methyl acrylate in [D_7]DMF at 22°C. – a) *t* ca. 2 min, b) *t* ca. 2 h, c) *t* ca. 72 h
1 = signals of **1**, Ma = signals of methyl acrylate, B = signals of 2,2′-bipyridine, L = solvent signals, Bu = signals of butane, E = ethene signal

Similarly the influence of added 2,2′-bipyridine to the decomposition of **1** in the presence of methyl acrylate was studied. At a molar ratio of 1:1867 of complex **1** to methyl acrylate different amounts (1, 5, and 10 equivalents) of 2,2′-bipyridine were added. The change in absorbance as a function of time is displayed in Fig. 4. No simple relationship can be recognized.

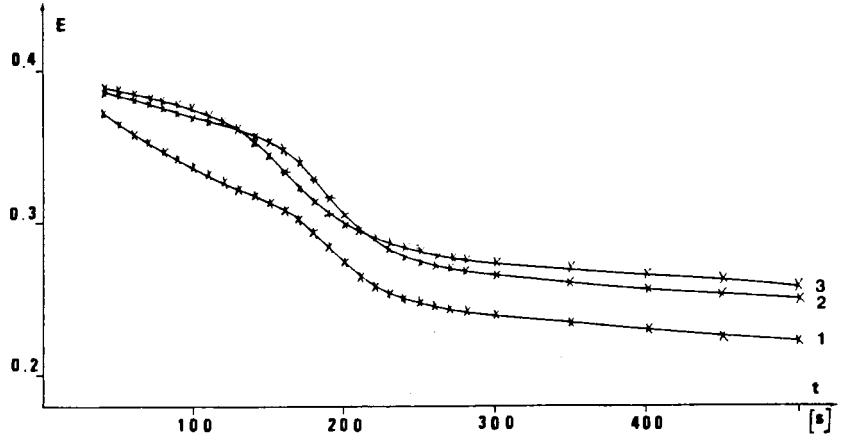


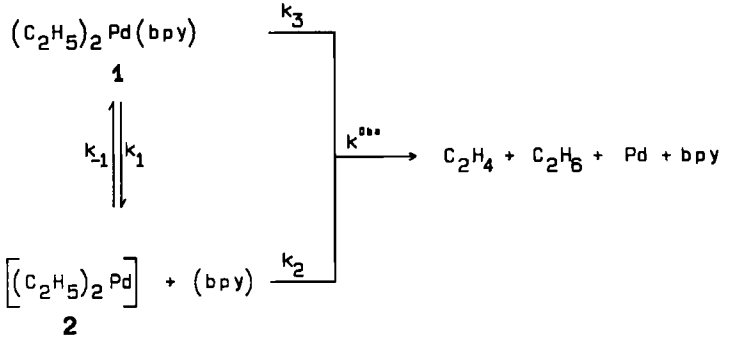
Fig. 4. Plot of extinction E vs. time for the reaction of **1** (0.0015 M) with methyl acrylate (2.8 M) and varying amounts of 2,2′-bipyridine (1 = 0.0016 M, 2 = 0.0075 M, 3 = 0.016 M)

The decrease in extinction during the reaction is slowed down by addition of 2,2′-bipyridine. It should be noted that there are also changes in product composition, if 2,2′-bipyridine is present in the system. We analyzed the products as a function of time in the presence of excess 2,2′-bipyridine. Table 4 discloses that within a short period of time almost all of the *n*-butane is formed. At later stages mainly ethane is generated, lowering the relative amounts of ethene and butane. This shows that several processes take place which may not be independent from each other.

Discussion

Thermolysis of (2,2′-bipyridine)diethylpalladium(II) (**1**) without an additive leads to identical results whether performed with or without solvent. A DSC analysis showed that there is no phase transition in the solid prior to decomposition. We can therefore assume as certain that it is the square planar d^8-complex which undergoes reaction and that there is no labilisation of the complex due to geometrical rearrangement. The formation of ethane and ethene is not a reaction of free radicals formed by homolytic cleavage of palladium carbon bonds. As the ratio of disproportionation to combination for ethyl radicals in solution is 0.14[17] a much higher proportion of butane would be expected in that case.

The dependence of the overall rate constant k_{obs} from the presence of additional 2,2′-bipyridine (Fig. 1) shows that the products ethane and ethene are formed by two competitive pathways:



Under the assumption that the intermediate **2** exists in a steady state concentration the rate equation for the disappearence of **1** can be written as:

$$-\frac{d[1]}{dt} = [1]\left[\frac{k_1 \cdot k_2}{k_{-1}[bpy] + k_2} + k_3\right]$$

At low concentration of 2,2′-bipyridine k_{obs} corresponds to $k_1 + k_3$, i.e. product formation takes place *via* ligand dissociation and *via* a direct process. If ligand dissociation is suppressed k_{obs} approaches k_3. The rate decrease in the presence of 2,2′-bipyridine shows that decomposition via ligand dissociation should be the energetically preferred route for product formation. It should be noted that due to the evolution of 2,2′-bipyridine during the decomposition the measured rate constants in the absence or presence of low additional amounts of 2,2′-bipyridine constitute averaged values with respect to the changing amount of 2,2′-bipyridine. However this does not alter the conclusions.

In an elegant investigation on diethylbis(tert. phosphane)palladium(II) complexes *Yamamoto* discovered that the geometrical arrangement of ligands is important for product formation[7]. The possibility for *cis* or *trans* arrangement which exists only for nonchelating ligands disclosed that reductive elimination with formation of *n*-butane takes place only in the *cis*-diethylbis(tert. phosphane)palladium(II) complexes. Interestingly addition of two equivalents of phosphane provides a change to disproportionation products[18]. This suggests a dissociative process for *n*-butane formation and a nondissociative one for ethane/ethene evolution[7,14,18]. With 2,2′-bipyridine as ligand on diethylpalladium(II) both dissociative and nondissociative thermolysis leads to disproportionation products. In this respect there are similarities to *cis*-diethylbis(triethylphosphane)platinum(II)[19] which produces only ethane/ethene on thermolysis. A thorough analysis of the mechanism by which ethane and ethene are produced showed that there are three different ways with three different rate determining steps[19]. Dissociative and nondissociative pathways are involved depending on the amount of additional ligand.

The mechanistic picture changes if electron deficient olefins are added. (2,2′-Bipyridine)diethylpalladium(II) (**1**) generates almost exclusively *n*-butane. An in-

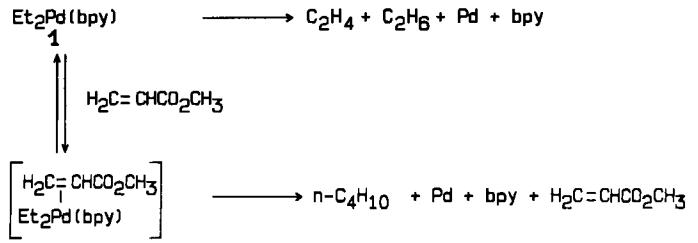
fluence of added olefin for product formation allegedly does not exist for diethylbis(tert. phosphane)palladium(II)[7,14]. Presumably the olefin traps only a divalent bis(tert. phosphane)palladium(0) species after reductive elimination. This interpretation, however, does not provide consistent mechanistic pictures.

In view of the observations for (2,2′-bipyridine)diethylpalladium(II) (**1**) the results for the tert. phosphane complexes might be reconciled if an influence of added olefin is admitted. The complete reversal in product composition on addition of methyl acrylate to **1** together with the kinetic measurements of its participation in the rate determining step for decomposition proves its importance for the reaction. This is also in line with results for the thermolysis of (2,2′-bipyridine)diethylnickel(II)[11]. Recent measurements showed here that only in the presence of electron deficient olefins reductive elimination is the exclusive pathway[15]. It is interesting to note that the (2,2′-bipyridine)diethylnickel(II) complex yields products of reductive elimination and disproportionation in a 1:1 ratio if thermolyzed in the absence of an additive.

Puddephatt[20] showed that the (2,2′-bipyridine)diethylplatinum(II) complex exhibits yet another picture. An analysis of thermolytic reactions similar to those presented here showed no reductive elimination even in the presence of added olefin. Due to the possibility of 2,2′-bipyridine dissociation after association of methyl acrylate this complex still has a pathway for β-hydrogen elimination.

A rationalisation of the results on the decomposition of (2,2′-bipyridine)diethylpalladium(II) (**1**) might be as follows (Scheme 1): In terms of electron counting it constitutes a 16 electron complex. Thus there should be the possibility to add a further ligand with formation of an 18 electron complex. If no external ligand is added this position is available for a β-hydrogen atom leading to the formation of disproportionation products. In the presence of an electron deficient olefin this position is blocked and reductive elimination is observed. This, in addition, is accompanied by a decrease in activation energy for decomposition.

Scheme 1



The fascination, which originates from the comparison of the behavior of complexes which differ only in the d^8-metal atom, has led to interesting insights. Thus there seems to be a decrease in ease of reductive elimination within a group of elements in the periodic table, a result which was rationalized theoretically[21–23].

This work was supported by the *Dr.-Jost-Henkel-Stiftung* and the *Fonds der Chemischen Industrie*. We are grateful to Dr. *H.-G. Korth* for discussions concerning the evaluation of the kinetic data.

Experimental Part

All reactions and the kinetic measurements were carried out under argon. Solvents were thoroughly dried by distillation from sodium/potassium alloy and were saturated with argon.

^{1}H NMR spectra: Varian XL-200 spectrometer. – UV spectra: Cary 219 spectrometer. – Gas analyses: GLC with a plot fused silica (Al_2O_3) capillary column (50 m). Gases, evolved during decomposition of metal complexes, were collected with a Toepler pump. Yields of gaseous products were obtained by measuring the gas pressure within a defined volume with a mercury manometer. For reactions in solution the gases were removed from the solvent by repeated freeze/thaw cycles prior to the determination of the yield of gaseous products.

(2,2'-Bipyridine)diethylpalladium(II) (**1**): 2.9 g (10 mmol) of (acetylacetonato)palladium (Ventron) and 3.0 g (20 mmol) of 2,2'-bipyridine were suspended in 50 ml dry diethyl ether. After addition of 4.3 ml (29 mmol) of diethylaluminum ethoxide the yellow suspension was stirred for 4 d at 22°C. The brownish suspension was filtered over a Schlenk frit (G 3), the brown solid was washed three times with 5 ml of dry diethyl ether and dried in vacuo (ca. 1.3 Pa). The raw crystals (2.1 g) were extracted on a Soxhlet apparatus with 50 ml of acetone under reduced pressure (ca. 9.3 kPa ≙ 70 Torr). After 24 h extraction the dark red solid was separated with a Schlenk frit (G 3) and dried in vacuo (0.013 Pa). Yield: 0.80 g (26%). The yield increases to 67% by workup of the acetone solution. m.p. 109°C (dec.). – IR (KBr): 2830 and 2930 (CH), 1310 and 755 cm^{-1} (bpy[24]). – UV (THF): λ_{max} (lg ε) = 496 (ca. 2.5), 367 (ca. 3.3), 280 (ca. 4.14), 248 nm (ca. 4.07). – ^{1}H NMR ([D_7]DMF): δ = 1.2 (10H, mc, C_2H_5), 7.75 (2H), 8.15 (2H), 8.54 (2H), and 8.80 (2H) (2,2'-bipyridine).

$C_{14}H_{18}N_2Pd$ (320.7)	Calcd.	C 52.43	H 5.65	N 8.73	Pd 33.18
	Found	C 52.37	H 5.79	N 8.99	Pd 33.08

Thermolysis of (2,2'-Bipyridine)diethylpalladium(II) (**1**): 0.077 g (0.24 mmol) of complex **1** was heated for 30 min at 110°C in an evacuated Schlenk apparatus (p = 0.13 Pa) which was connected with a high vacuum line and a Toepler pump. The solid residue consisted of black palladium and colorless crystals of 2,2'-bipyridine. GlC analysis: 44% ethene, 51% ethane, 3% *n*-butane, traces < 1.5% isomers of butene, total yield: 94%.

Thermolysis of **1** *in Diphenylmethane:* 0.067 g (0.21 mmol) of **1** was suspended in 3.0 ml of diphenylmethane. The Schlenk apparatus was cooled in liquid nitrogen and evacuated. After warming to room temp. the solution was heated for 4 h at 80°C in an oil bath. During this time the colour of the solution changed from red to light yellow and black palladium deposited. GLC analysis: 45% ethene, 53% ethane, 2% *n*-butane, traces < 1%, methane, propane, propene, and butene isomers, total yield: 70%.

Thermolysis of **1** *in Benzene in the Presence of 10 equ. of 2,2'-Bipyridine:* 0.104 g (0.33 mmol) of **1** and 0.520 g (3.3 mmol) of 2,2'-bipyridine were dissolved in 3 ml of benzene. The reaction vessel was cooled with liquid nitrogen and evacuated. After warming up the solution was heated for 5 h at 80°C (oil bath). The colour of the solution changed from red to greenish-yellow during this time and black palladium deposited. GLC analysis: 45% ethene, 54% ethane, 1% butane, total yield: 61%.

Reaction of **1** *with Methyl Acrylate:* To 0.291 g (0.91 mmol) of **1** in an evacuated Schlenk vessel was added at 25°C a mixture of 0.8 ml (9.1 mmol) of methyl acrylate and 3.0 ml of diphenylmethane. During reaction (20 h at room temp.) the colour of the solution changed from red to greenish-black and a black solid deposited. GLC analysis: 8% ethene, 3% ethane, 89% *n*-butane, total yield: 100%.

Kinetics of Decomposition of **1** *by ^1H NMR:* The kinetic measurements were performed in a Varian XL-200 spectrometer with variable temperature unit (± 2.5°C). To 0.1 M solutions of **1** in [D_7]DMF was added the respective amount of 2,2'-bipyridine (see table 2) and the change of the concentration of **1** with time was monitored by signals of the ethyl protons at 1.25 ppm. As internal standard we used the proton signal of residual undeuterated DMF. For individual runs between 6 and 13 points served as basis for the evaluation of the rate constants.

Kinetics of the Reaction of **1** *with Methyl Acrylate by UV Spectroscopy:* The reaction of **1** with methyl acrylate at 22 ± 2°C was followed UV spectroscopically at 496 nm. 1.5 ml of a 0.002 M solution of **1** in THF was combined with 0.5 ml of the corresponding solution of methyl acrylate in THF immediately before the measurement in a special cell under argon. Methyl acrylate was used in 367–1867 fold excess relative to **1**. The evaluation of the rate constants, based on 17 data points for each run, by a nonlinear regression analysis took account of a rest absorption which was assumed to be formed during the reaction by a first order process. This absorption originates probably from an intermediate complex (2,2-bipyridine)(methyl acrylate)palladium[25] which decomposes slowly to the organic compounds and metallic palladium. None of the compounds absorbs at 496 nm. The high concentration of methyl acrylate secured reaction times during which negligable palladium metal deposited.

CAS Registry Numbers

1: 102150-17-4 / $Pd(acac)_2$: 14024-61-4 / 2,2'-bipyridine: 366-18-7 / methyl acrylate

[1] *U. Bayer* and *H. A. Brune*, Z. Naturforsch., Part B **38**, 621 (1983).
[2] *A. Goliaszewski* and *J. Schwartz*, J. Am. Chem. Soc. **106**, 5028 (1984).
[3] *P. W. Jolly*, Angew. Chem. **97**, 279 (1985); Angew. Chem., Int. Ed. Engl. **24**, 283 (1985).
[4] *M. F. Semmelhack, P. M. Helquist*, and *J. D. Garzynski*, J. Am. Chem. Soc. **94**, 9234 (1972).
[5] *A. Gillie* and *J. K. Stille*, J. Am. Chem. Soc. **102**, 4933 (1980).
[6] *A. Moravskiy* and *J. K. Stille*, J. Am. Chem. Soc. **103**, 4182 (1981).
[7] *F. Ozawa, T. Ito, Y. Nakamura*, and *A. Yamamoto*, Bull. Chem. Soc. Jpn. **54**, 1868 (1981).
[8] *P. Diversi, D. Fasce*, and *R. Santini*, J. Organomet. Chem. **269**, 285 (1984).
[9] *G. M. Whitesides*, Pure Appl. Chem. **53**, 287 (1981).
[10] *A. Yamamoto, T. Yamamoto, S. Komiya*, and *F. Ozawa*, Pure Appl. Chem. **56**, 1621 (1984).
[11] *T. Yamamoto, A. Yamamoto*, and *S. Ikeda*, J. Am. Chem. Soc. **93**, 3350 (1971).
[12] *T. Saito, Y. Uchida, A. Misono, A. Yamamoto, K. Morifuju*, and *S. Ikeda*, J. Am. Chem. Soc. **88**, 5198 (1966).
[13] *G. Wilke* and *G. Herrmann*, Angew. Chem. **78**, 591 (1966); Angew. Chem., Int. Ed. Engl. **5**, 581 (1966).
[14] *F. Ozawa, T. Ito*, and *A. Yamamoto*, J. Am. Chem. Soc. **102**, 6457 (1980).
[15] *J. Lau* and *R. Sustmann*, Tetrahedron Lett. **26**, 4907 (1985).
[16] *T. Yamamoto, Y. Nakamura*, and *A. Yamamoto*, Bull. Chem. Soc. Jpn. **49**, 191 (1976).
[17] *D. C. Nonhebel* and *J. C. Walton*, Free-radical Chemistry, p. 134, Cambridge University Press 1974.
[18] *F. Ozawa, K. Kurihara, T. Yamamoto*, and *A. Yamamoto*, Bull. Chem. Soc. Jpn. **58**, 399 (1985).
[19] *T. J. Mc Carthy, R. G. Nuzzo*, and *G. M. Whitesides*, J. Am. Chem. Soc. **103**, 3396 (1981).
[20] *N. Chaudhury* and *R. J. Puddephatt*, J. Chem. Soc., Dalton Trans. **1976**, 915.
[21] *K. Tatsumi, R. Hoffmann, A. Yamamoto*, and *J. K. Stille*, Bull. Chem. Soc. Jpn. **54**, 1857 (1981).
[22] *K. Tatsumi, A. Nakamura, S. Komiya, A. Yamamoto*, and *T. Yamamoto*, J. Am. Chem. Soc. **106**, 8181 (1984).
[23] *A. C. Balazs, K. H. Johnson*, and *G. M. Whitesides*, Inorg. Chem. **21**, 2162 (1982).
[24] *S. Herzo, K. Klausch*, and *J. Lantz*, Z. Chem. **4**, 150 (1964).
[25] *R. Sustmann, J. Lau*, and *M. Zipp*, Rec. Trav. Chim. Pays-Bas, in press.

[47/86]