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DIETHYL-2,2'-BIPYRIDYL-PALLADIUM(II), A CASE FOR THE STUDY OF COMBINATION VS. DISPROPORTIONATION PRODUCTS.

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Abstract: Diethyl-2,2'-bipyridyl-palladium(II) is synthesized and its decomposition reactions in absence and presence of methyl acrylate are compared with those of the corresponding nickel and platinum complexes. Depending on the reaction conditions either CC-coupling or disproportionation can be induced.

Reactions of diethyl-transition metal complexes of d^8-elements which are important as elementary processes in homogeneous catalysis, have been studied extensively [1-14]. With respect to CC-coupling it is important to know the factors by which the undesired disproportionation products can be eliminated. The nature of the transition metal must be of special importance in this context as is demonstrated by the reactions of diethyl-2,2'-bipyridyl-nickel(II) [1-4], yielding mainly butane on thermolysis and diethyl-2,2'-bipyridyl-platinum(II) [5,6] which is reported to give only ethane/ethene on thermolysis. In order to learn about the role of the transition metal we prepared and studied the analogous palladium complex.

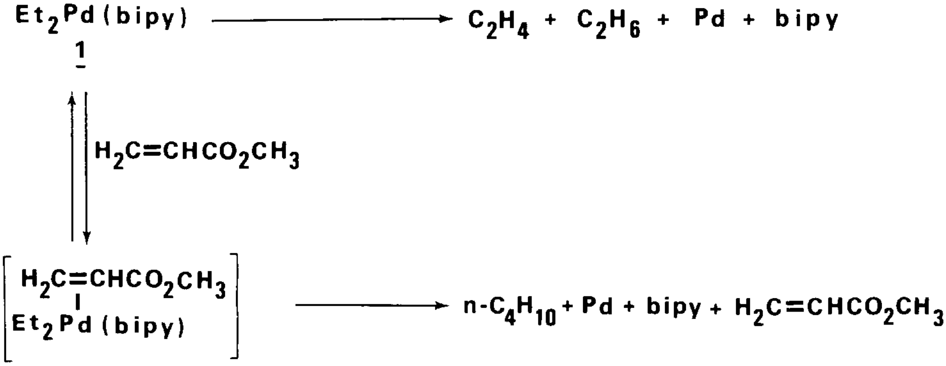
Diethyl-2.2'-bipyridyl-palladium(II) (1) was prepared in analogy to the nickel complex [1] from palladium acetylacetonate (9.5 mmol), 2,2'-bipyridyl (19 mmol) and monoethoxy diethylaluminum (29 mmol) in 25 ml absol. diethyl ether. After four days at room temperature, the precipitate was extracted with acetone in a soxleth apparatus under reduced pressure and 67% 1 were obtained as red crystals with mp. 109° (decomp.) [16]. This complex was subjected to thermolysis, neat or in solution, in absence and in presence of additives. Where necessary and for the purpose of comparison experiments with the analogous nickel and platinum complexes were performed.

Thermal decomposition [17] of diethyl-2,2'-bipyridyl-nickel(II) yields a 1:1

ratio of butane and ethane/ethene (table 1). Disproportionation products, liberated in an almost 1:1 ratio, dominate in the decomposition of the palladium complex. The platinum complex produces exclusively ethane and ethene with predominance of the former. The smaller total yield of gaseous products for the platinum complex is explained with the formation of polymeric material. Comparable results are obtained if the complexes are thermolyzed in benzene or diphenylmethane. The important observation is the change from a mixture of butane and ethane/ethene to ethane/ethene as sole products if the central metal atom is varied from nickel over palladium to platinum.

The complexes exhibit also different reactivity in presence of additives. Diethyl-2,2'-bipyridyl-nickel(II) does show a change in product composition to almost exclusive formation of butane if methyl acrylate is added, which confirms the results of Yamamoto [2]. The palladium complex now also provides in high yield butane. As was found earlier [6] the platinum complex liberates ethene in presence of methyl acrylate. As organometallic products were identified a mixture of mono and bis(methyl acrylate)-2,2'-bipyridyl-nickel [2] and bis(methyl methylacetate)-2.2'-bipyridyl-platinum(II) [6]. A complex of methyl acrylate with palladium bipyridyl could not be isolated. However, with more electron deficient olefins, like fumaronitrile and diethyl fumarate, 1:1 complexes are obtained [18]. It is assumed that the corresponding methyl acrylate complex is unstable under the reaction conditions. This is supported by the formation of elemental palladium in this reaction.

Scheme 1



The influence of methyl acrylate on the reaction course points to an associative mechanism for the formation of butane according to the reaction scheme. The possibility to induce CC-coupling in a case where β-hydrogen atoms are present in the alkyl groups may be of importance in palladium catalyzed reactions. Further studies concerning the mechanism and the scope of these reactions are in progress.

Table 1. Reactions of diethyl-2,2'-bipyridyl-d^8-transitionmetal complexes.

complex[a]	additive[b]	solvent	T[°C]	reaction time [h]	ethene [%]	ethane [%]	butane [%]	total[c] yield [%]
Et_2Ni(bipy)	-	-	130	0.5	20	28	52	103
Et_2Ni(bipy)	-	$(Ph)_2CH_2$	130	3	15	28	57	85
Et_2Ni(bipy)	ma[d]	$(Ph)_2CH_2$	25	3	7	1	92	87
Et_2Ni(bipy)	ma[d]	$(Ph)_2CH_2$	130	0.5	14	2	84	84
Et_2Pd(bipy)	-	-	110	0.5	44	51	3	94
Et_2Pd(bipy)	-	C_6H_6	80	4	45	53	2	70
Et_2Pd(bipy)	ma[d]	$(Ph)_2CH_2$	25	20	8	3	89	100
Et_2Pd(bipy)	ma[d]	$(Ph)_2CH_2$	80	0.5	16	3	81	102
Et_2Pd(bipy)	bipy[e]	C_6H_6	80	5	45	54	1	60
Et_2Pt(bipy)	-	-	130	0.5	21	79	-	70
Et_2Pt(bipy)	-	$(Ph)_2CH_2$	130	3	24	76	-	68
Et_2Pt(bipy)	ma[d]	-	50	6	97	3	-	74
Et_2Pt(bipy)[6]	ma[d]	-	50	6	100	-	-	91

a) ca. 1 mmol complex, b) 5-10 fold M excess, c) total yield (mol/mol complex) = [0.5(R-H + RH) + RR]/(complex), error limits ± 5%, d) methyl acrylate, e) 2.2'-bipyridyl

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16. Anal. Calcd. for $C_{14}H_{18}N_2Pd$:C, 52.43, H, 5.65, N, 8.73, Pd, 33.18. Found: C, 52.37, H, 5.79, N, 8.69, Pd, 33.08. ^{1}H-NMR ($(D_3C)_2CO$):8.80(d,2H), 8.45 (d,2H), 8.15(t,2H), 7.75(t,2H), 1.2(m,10H). UV/Vis (THF): 496 nm (ε= 300), 367 nm (ε = 2200).
17. Reactions were carried out on a high vacuum line connected with a Töpler pump. Gases were analyzed by GLC with a Plot Fused Silica (Al_2O_3) capillary column.
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