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PRELIMINARY COMMUNICATION

THE HYDROLYSIS OF π-ALLYLPALLADIUM COMPLEXES IN DILUTE BASE - EVIDENCE FOR DISPROPORTIONATION OF THE π-ALLYL GROUP

T.A. SCHENACH and F.F. CASERIO, Jr.
ARCO Chemical Company, Anaheim, California (U.S.A.)

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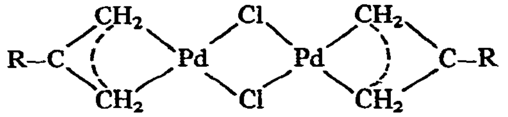
The disproportionation of cyclohexenes to cyclohexanes and aromatics occurs readily at room temperature over heterogeneous palladium catalysts[1]. We have now observed similar behavior with π-(allyl)palladium chloride dimers (Ia and Ib) in a homogeneous system.



(Ia, R = CH_3:
Ib, R = H)

Hüttel and co-workers[2] have reported the facile hydrolysis of Ia to isobutylene and methacrolein in boiling 0.1*N* sodium hydroxide. Both Ia and Ib dissolve readily in aqueous base, yielding yellow solutions which decompose slowly on standing and rapidly on heating. Acidification reprecipitates the complexes. To obtain NMR data, we dissolved Ia and Ib in sodium deuteroxide–deuterium oxide. The spectra are listed in Table 1, and are similar to those of Ia and Ib in nonaqueous solvents, suggesting that the π-allyl type bonding is retained. Even on warming the solutions to their decomposition point (~ 80°), no σ-allyl absorptions were seen.

Heating a 0.22*M* solution of Ia in NaOD–D_2O (2 moles of OD^- per mole of Ia) caused rapid formation of a palladium mirror and evolution of isobutylene in 63% yield. The amount of deuterium incorporated in the gas was determined by mass spectrometry and infrared analysis. The result was quite unexpected. Although NMR indicated less than 2 mole % H_2O in the original solution, the isobutylene liberated was over 93% undeuterated (7% C_4H_7D, trace of $C_4H_6D_2$). Likewise, heating a 0.2*M* solution of Ib in NaOD–D_2O (containing less than 0.5 mole % H_2O) evolved propylene in 58% yield. In this case, 83% of the olefin was undeuterated (13% C_3H_5D, 3% $C_3H_4D_2$, traces of $C_3H_3D_3$ and $C_3H_2D_4$).

Evidently the major reaction that occurs is not a simple hydrolytic cleavage of the allyl–palladium bond, which should yield mainly monodeuterated olefins,

TABLE 1

NUCLEAR MAGNETIC RESONANCE SPECTRA OF Ia and Ib[a]

Complex	Solvent	Absorption	τ	(Relative intensity)	
Ia	NaOD–D_2O	Singlet	7.8	(3)	
		Singlet	7.4	(2)	
		Singlet	6.4	(2)	
Ia	$CDCl_3$[6]	Singlet	8.2	(3)	
		Singlet	7.4	(2)	
		Singlet	6.5	(2)	
Ib	NaOD–D_2O	Doublet	7.1	(J 12 cps)	(2)
		Doublet	6.1	(J 7 cps)	(2)
		Multiplet	4.4	(1)	
Ib	Benzonitrile[3]	Doublet	7.0	(J 12 cps)	(2)
		Doublet	6.0	(J 7 cps)	(2)
		Heptet	4.6	(1)	

[a] Spectra taken on a Varian A60 60 MHz Spectrometer with tetramethylsilane as external standard. Two moles of sodium deuteroxide per mole of complex were used to prepare the D_2O solutions.

$CH_2{=}C(R)CH_2D$★. Instead the π-allyl groups must have abstracted hydrogen from an adjacent allyl group, forming the unlabeled olefin and dehydrogenated product★★. This fragment may simultaneously or subsequently add water and/or atmospheric oxygen to yield the other products which are observed - methacrolein from Ia, allyl alcohol from Ib.

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★Although there is enough H_2O present to form the amounts of undeuterated olefins we observed, in view of the vast excess of D_2O, the magnitude of the isotope effect necessary would be enormous ($k_{H_2O}/k_{D_2O} \sim 10^3$). Hence we prefer the dehydrogenation mechanism proposed below.

★★A dehydrogenated allyl group has been postulated as an intermediate in the reaction of allene with $(C_6H_5CN)_2PdCl_2$[3], and in the catalytic oxidation of propylene to acrolein.[4]