The Role of Dimethylformamide in the Interaction of Olefins with Palladium Chloride. [A New Method of Synthesis in Mild Conditions of π-Allylpalladium(II) Compounds]

By (the late) D. MORELLI, R. UGO,*† F. CONTI, and M. DONATI

(*Istituto di Ricerche di Base "G. Donegani", Montecatini Edison S.p.A., Milano, and †Istituto di Chimica Generale dell'Università, Milano, Via C. Saldini* 50)

π-ALLYL compounds of palladium(II) with formula (π-$C_nH_{2n-1}PdCl)_2$, known for many years,[1] can be synthesized by various routes. From mono-olefins and palladium(II) salts, the π-allyl compounds could only be obtained by thermal methods at a temperature above 60°.[2,3]

Whilst studying the interaction and isomerization of straight-chain α-olefins with $PdCl_2$,[3–5] with different solvents, we found that, unlike in other solvents, the isomerization of the olefins (but-1-ene, pent-1-ene, hex-1-ene, and oct-1-ene) in dimethylformamide (DMF) at room temperature proceeded only partially (*e.g.*, but-1-ene in a ratio of olefin to $PdCl_2$ of 4 : 1, the isomerization after 5 hr. was only 40%). Finally two stable compounds were formed; a yellow and a brown one, which were recovered after evaporation *in vacuo* of the excess of DMF and olefin. The yellow compound, soluble in light hydrocarbons, varied with the olefin and was identified by analysis (i.r. and n.m.r. spectra) as belonging to the known type (π-$C_nH_{2n-1}PdCl)_2$,[2,3] while the insoluble, brown substance which was the same irrespective of the olefin used, must originate from the solvent. This is confirmed by the i.r. spectrum, where a broad carbonyl stretching of the amide was found at 1630 cm.$^{-1}$ and in the range 1600—600 cm.$^{-1}$ a strong broad absorption was present with large "transmission windows" at 855 and 630 cm.$^{-1}$. This spectrum did not correspond to that of the compounds $PdX_2(DMF)_2$,[6] but was consistent with the presence of the cation $[(DMF)_2H]^+$ formed by a hydrogen ion symmetrically bonded between the two carbonyl groups.[7-10]

The analysis agreed with the formula $[(DMF)_2H]_2[Pd_2Cl_6]$ which was confirmed in the following way:

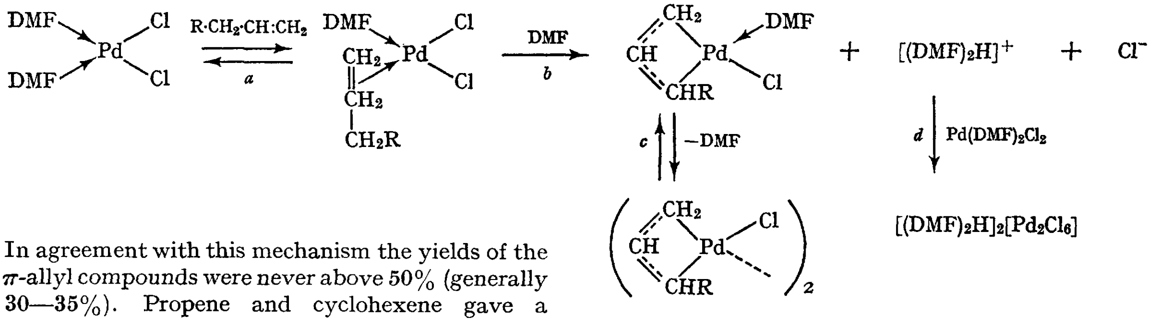
(a) The presence of terminal and bridging Pd–Cl stretching at 400 and 315 cm.$^{-1}$;

(b) The conductivity in nitrobenzene which was consistent with a 2:1 type ($\Lambda = 79 - 445\sqrt{c}$) electrolyte;[11]

(c) The formation by double exchange of $[N(Bu^t)_4]_2[Pd_2Cl_6]$ and $[AsPh_4]_2[Pd_2Cl_6]$ both characterized by analysis and electronic spectra;[12]

(d) The preparation of the same compound on bubbling hydrogen chloride in a dimethylformamide solution of $PdCl_2$.

The mechanism of the reaction is possibly:



In agreement with this mechanism the yields of the π-allyl compounds were never above 50% (generally 30—35%). Propene and cyclohexene gave a similar reaction, though without the isomerization, and $PdBr_2$ reacted as $PdCl_2$.

Probably DMF on account of the particularly stable hydrogen bond favours the HCl abstraction, so that the formation of the π-allyl compounds is easier than in the other solvents.

The presence of the intermediate unstable π-complex (step *a*), which in the other solvent is considered to be the first stage of the isomerization, was proved by the isolation at −80° of very unstable π-complexes of palladium formed by reaction of $Pd(DMF)_2Cl_2$[6] with an excess of olefin. These complexes, which still have a molecule of DMF co-ordinated to the palladium atom, are quickly transformed into the π-allyl derivatives (shown by n.m.r. spectroscopy).

To confirm the suggested mechanism, we have used $PtCl_2$ under the same conditions as $PdCl_2$; a yellow compound, $Pt(olefin)(DMF)Cl_2$ was isolated in the case of pent-1-ene (m.p., 65° decomp.): the presence of a π-bonded olefin in this compound, which is fairly stable, was confirmed by the n.m.r. spectrum (CCl_4) at room temperature, which shows two series of peaks characteristic of DMF and of pent-1-ene co-ordinated to the metal. Three peaks of intensity 1:3:3 at τ 1·88, 6·90, and 7·00 were assigned to formyl and methyl protons. Four broad peaks of intensity 1:2:4:3 at τ 4·70, 5·60, 8·15, and 8·90 were assigned to the unsaturated methine and methylene, to the two saturated methylenes, and to the methyl groups.

The same compound was more easily obtained by treating $Pt(DMF)_2Cl_2$ with an excess of the olefin at room temperature.[6] The olefin was lost by heating either *in vacuo* or in DMF solution.

The π-allyl compound of platinum(II) has not yet been obtained by a similar reaction in DMF, on account of the greater stability of the π-platinum–ethylenic compounds.

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