Arylation of Alkenyl Bromides Catalysed by Platinum Complexes

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Biphosphine platinum complexes catalyse the cross-coupling of arylmagnesium halides and arylethenyl bromides under mild conditions.

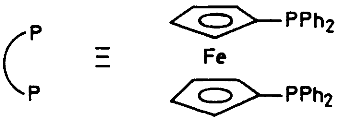
In recent studies on the mechanism of palladium-catalysed cross-coupling reactions,[1] it proved impossible to observe the penultimate intermediate (**1a**) because C–C elimination occurred readily at −78 °C. Alkylplatinum complexes possess much greater thermal stability than their Pd or Ni analogues.[2] For this reason they have generally been considered to be too inert for catalytic application, albeit useful as isostructural models for reactive intermediates. We report the first examples of efficient Pt-catalysed cross-coupling, based on our observations of the thermolabile (**1b**).

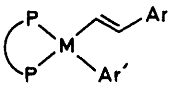
Following earlier protocols,[3] the η^2-ethylene complex (**2a**) was prepared from the corresponding $PtCl_2$ biphosphine complex. The reaction with halide (**3**) occurred in tetrahydrofuran (THF) at ambient temperature giving an isolable alkene complex (**4**) contrasting with the easy insertion/rearrangement observed in the palladium case.[1] On standing the THF solution (20 °C; 7 d) complete conversion into the alkenyl bromide complex (**5**) was observed; reaction was readily monitored by ^{31}P n.m.r. spectroscopy. In contrast, the reaction in CH_2Cl_2 was complete within minutes, and we suspected the intervention of electron-transfer catalysis,[4] since chlorinated solvents are known to oxidise Pt complexes.[5] Further evidence was obtained by conducting the reaction in THF in the presence of a trace (*ca.* 10^{-5} M; 0.1%) of $AgSO_3CF_3$, a well-established 1-electron oxidant.[6] This reduced the time for complete reaction at 20 °C from 7 days to 10 minutes.

It was ascertained that the η^2-alkene complex (**4**) did not react readily with arylmagnesium halides in THF. Complex (**5**) was immediately converted into the aryl alkenyl complex (**6**) in THF on addition of *o*-$CH_3OC_6H_4MgBr$. To our surprise, this was unstable in solution at ambient temperature and had part-rearranged to the η^2-alkene complex (**7**) [which could be synthesised independently from the stilbene and

Table 1. ^{31}P N.m.r. spectral data for platinum complexes in THF at ambient temperature.

	γ(P_A)	δ(P_B)	$J(P_APt)$	$J(P_BPt)$	J(PP)
(2a)	25.1	—	3704	—	—
(2b)	23.1	—	3736	—	—
(4)	21.6	20.3	3421	3499	30
(5)	12.8	12.5	1712	4346	10
(6)	16.2	12.2	1912	1965	16
(7)	22.6	21.1	3779	3780	43
(8)	18.8	15.0	1900	1748	16
(9)	22.1	22.1	~3730	~3730	—





(1) a; M = Pd
b; M = Pt

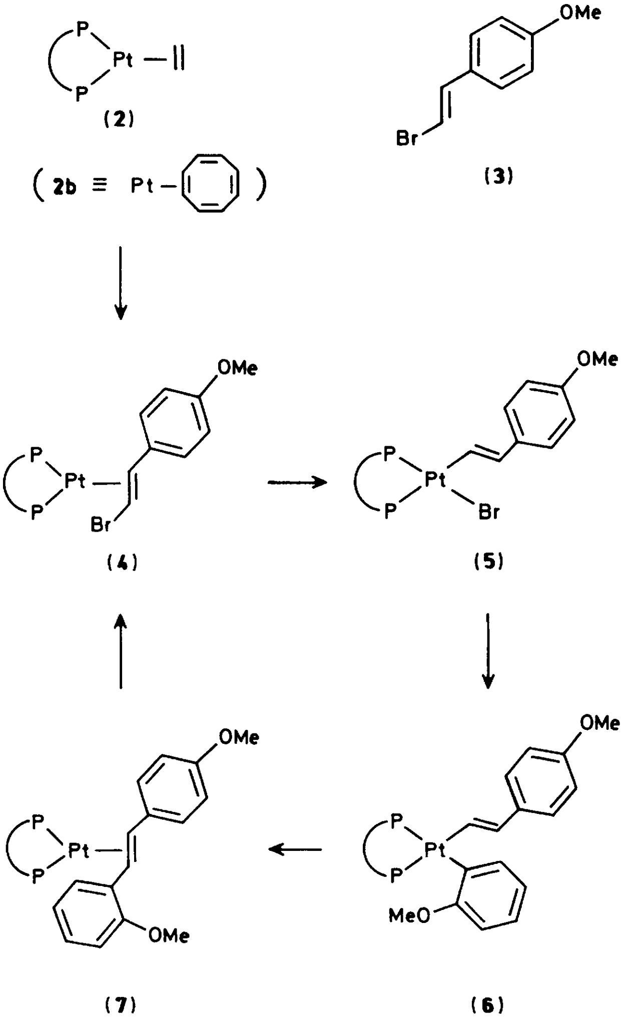
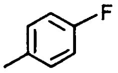
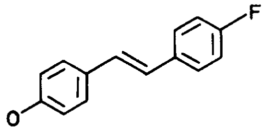
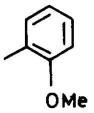
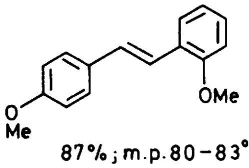
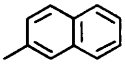
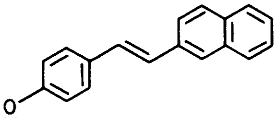
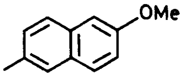
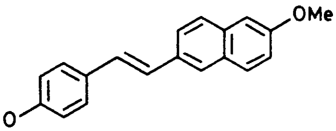
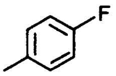
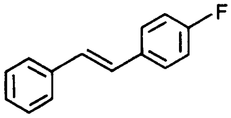
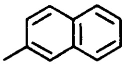
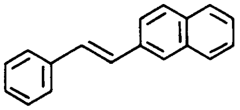
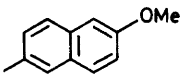
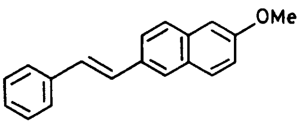


Table 2. Catalytic cross-coupling using 2 mole % (**4**) as catalyst in THF, 2 d, reflux.

RMgBr	Product[a]
	 95%; m.p. 138 – 140°C
	 87%; m.p. 80 – 83°C
	 94%; m.p. 159 – 162°C
	 80%; m.p. 182 – 185°C
	 94%; m.p. 102 – 104°C
	 92%; m.p. 128 – 130°C
	 91%; m.p. 147 – 149°C

[a] First four entries using (**3**), remainder using E-PhCH=CHBr.

complex (**1**)]. The half-life was <1 h at 30 °C. Entirely similar observations were made using PhMgBr [leading through complex (**8**) to η^2-alkene complex (**9**)] or p-FC_6H_4MgBr, but in these cases rearrangement was a factor of 2—4 times slower. Such mild conditions for C–C elimination at platinum are without precedent; alkyl complexes are rather inert, and biaryl (bis)phosphine complexes require sustained heating above 80 °C to effect the reaction.[7] The crucial feature is the platinum–ethenyl bond, for elimination may occur by migration of the aryl group to sp^2-carbon [*cf.* R–M–C≡O →

R–C(O)–M] rather than by concerted bond cleavage. A similar route has been proposed for the interconversion of η^2-C_2H_4 and η^1-H,η^1-C_2H_3 iridium complexes.[8]

This easy C–C elimination suggested the possibility of a full catalytic cycle, which was readily realised in practice. Since coupling of aryl and alkenyl groups may be brought about by one-electron oxidants,[9] it was deemed essential to employ high purity magnesium. Further, each example in Table 2 was subjected to a control experiment where the Pt complex was omitted, and this proved negative in all cases. Over 200 turnovers may be effected if less Pt complex is used and reaction proceeds, albeit rather slowly, at ambient temperature. The 1,1′-bis(diphenylphosphino)ferrocene ligand, known to be particularly effective in cross-coupling[10] is not a unique requirement. Replacement by the corresponding DIOP Pt (C_2H_4)† complex[3] led to comparably efficient catalysis.

Samples of the putative intermediates (**4**), (**5**), and (**6**), were employed as catalysts in the reaction between *p*-methoxyphenylethenyl bromide and *o*-methoxyphenylmagnesium bromide under the conditions of Table 2. In each case a good yield of product was formed, adding weight to the likely involvement of these complexes in catalysis. The reaction cycle is transparent, in that each intermediate is readily observable and has a finite lifetime under the reaction conditions. These observations run counter to the widely-held notion that catalysis preferentially proceeds through transient intermediates inaccessible to direct observation.[11]

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† DIOP = {[2,2-dimethyl-1,3-dioxolan-4,5-diyl)bis(methylene)]-bis(diphenylphosphine)}.

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