

Phase-transfer and Metal-complex Catalysis with Quaternary Ammonium Chlorometallates

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Quaternary ammonium chlorometallates were found to be highly efficient bifunctional metal-complex and phase-transfer catalysts.

We have found recently¹ that co-ordination compounds of the type $[ML_2Cl_2]^+Cl^-$ [$M = Fe, Rh, Ir; L = 2,2'$ -bipyridine (bipy), 1,10-phenanthroline (phen)] act as bifunctional catalysts. These compounds can take part in the phase-transfer of various anions because of the lipophilic organic ligands as well as in metal-complex catalysis due to the transition metal, *e.g.* C=C and C≡C bond hydrogenation. However, these complexes are less effective in two-phase reactions than the commonly used onium salts since the metal-complex cations are insufficiently lipophilic. Systems containing the transition metal in the anion, with a quaternary onium ion as the cation apparently possess an advantage in this case.

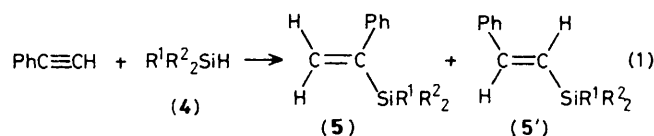
Compounds of the above type were prepared using two common routes for their synthesis,^{2,3} as exemplified by the complexes of Fe^{III}, Ir^{III}, and Pt^{IV}. For instance, $[Et_3NCH_2Ph][FeCl_4]$ (**1**) was prepared by reacting equimolar amounts of $FeCl_3 \cdot 6H_2O$ and triethylbenzylammonium chloride (TEBA) in ethanol. $[Et_3NCH_2Ph]_3[IrCl_6]$ (**2**) and $[Et_3NCH_2Ph]_2[PtCl_6]$ (**3**) were obtained as a result of ionic exchange between K_3IrCl_6 or K_2PtCl_6 and TEBA (1:3) in aqueous solution. TEBA is a readily available and in most cases sufficiently efficient phase-transfer catalyst.⁴ The results of elemental analysis obtained for complexes (**1**)–(**3**) corresponded to the expected composition. The ¹H n.m.r. spectra of (**2**) and (**3**) were similar to that of pure TEBA. The ¹H n.m.r. signals for complex (**1**) had the same values of chemical shifts, but were much broader owing to interaction between protons and the paramagnetic $FeCl_4^-$ ion.⁵

The bifunctional catalytic properties of the systems were tested in the hydrosilylation reaction of phenylacetylene with triethyl- and (dimethyl)phenyl-silane (metal-complex catalysis) followed by addition of dichlorocarbene generated in the

$CHCl_3/50\%$ aq. NaOH two-phase system (phase-transfer catalysis). The results of the reaction between phenylacetylene and silanes $R^1R^2_2SiH$ in the presence of complexes (**1**)–(**3**) and $H_2PtCl_6 \cdot 6H_2O$, a commonly used hydrosilylation catalyst, are summarized in Table 1. The formation of products of both α - and β -addition was observed in all cases, the latter being in the *trans*-configuration (equation 1).

The composition and structure of (**5a,b**) and (**5'a,b**) were assessed by ¹H n.m.r. and g.c.–mass spectrometry. Their ¹H n.m.r. parameters coincide with those given in the literature.^{6,7} Peaks of molecular ions were observed in the g.c.–mass spectra: m/z 218 [for (**5a**) and (**5'a**)] and 238 [for (**5b**) and (**5'b**)].

The experimental data show that the iridium and platinum complexes (**2**) and (**3**) are as efficient as the widely known platinum catalyst for hydrosilylation, the β -addition being predominant in both cases. The activity of catalyst (**1**) is somewhat lower and gives a different product ratio. The α -isomer prevails in reaction with Et_3SiH , whereas in the case of Me_2PhSiH the yields of α - and β -isomers are equal (Table 1). When the hydrosilylation reactions were terminated (controlled by g.l.c.), a tenfold molar excess of chloroform

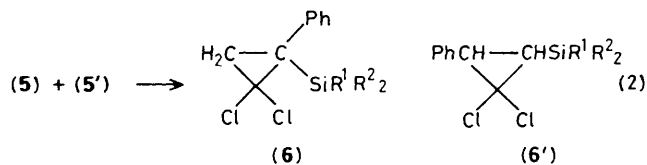


a; $R^1 = R^2 = Et$
b; $R^1 = Ph, R^2 = Me$

Table 1. Hydrosilylation of phenylacetylene.^a

Catalyst	Silane (4)	Reaction time, h	Product yield, % (g.l.c.)	
			α -Isomer (5)	β -Isomer (5')
$[Et_3NCH_2Ph][FeCl_4]$ (1)	(a)	1	10	5
		3	25	15
		5	50	20
		7	65	35
		1	25	25
		2	50	50
$[Et_3NCH_2Ph]_3[IrCl_6]$ (2)	(a)	1	20	80
		0.5	35	65
$[Et_3NCH_2Ph]_2[PtCl_6]$ (3)	(a)	1	40	60
		0.5	35	65
$H_2PtCl_6 \cdot 6H_2O$	(b)	0.5	40	60
K_2PtCl_6	(a)	1	2	2
$K_2PtCl_6 + [Et_3PhCH_2N]Cl$ (1:2)	(a)	1	15	18

^a Reaction conditions $PhC\equiv CH : R^1R^2_2SiH : catalyst = 1 : 1 : 0.001$; 120 °C.



Reagents: $\text{CHCl}_3/50\%$ aq. NaOH, catalyst (0.1 mol%).

was added to the resulting mixtures [(5a) + (5'a) and (5b) + (5'b)], containing catalysts (1)–(3), followed by dropwise addition of 50% aq. NaOH ($\text{CHCl}_3:\text{NaOH} = 1:1$), and stirring at room temperature. This initiated a two-phase process of dichlorocarbene generation and its addition at the double bond (equation 2).

For comparison, the same reactions were conducted under analogous conditions in the presence of TEBA. The activity of complexes (1)–(3) was similar to that of TEBA [in all cases a complete conversion of (5a) and (5'a) occurs during 1 h, (5b) and (5'b) during 3 h]. The adducts of (5a,b) and (5'a,b) with dichlorocarbene [(6a,b) and (6'a,b)] were obtained for the first time and identified by g.c.–mass and ^1H n.m.r. spectroscopy of the reaction mixtures.†

The addition of $:\text{CCl}_2$ to styrene in the presence of catalyst (1), and for comparison using TEBA, was performed under the same conditions. In both cases 100% conversion of styrene into 1,1-dichloro-2-phenylcyclopropane occurred during 30 min (according to g.l.c. data).

† ^1H n.m.r. spectra (CDCl_3 , 90 MHz), δ : (6a) 0.6–1.1 (m, 15H), 1.79 (d, 1H, J 6 Hz), 1.93 (d, 1H, J 6 Hz), 7.2–7.4 (m, 5H); (6'a) 0.6–1.1 (m, 15H), 1.18 (d, 1H, J 11 Hz), 2.76 (d, 1H, J 11 Hz); (6b) 0.38 (s, 6H), 1.82 (d, 1H, J 6 Hz), 2.00 (d, 2H, J 6 Hz), 7.1–7.5 (m, 10H); (6'b) 0.51 (s, 3H), 0.58 (s, 3H), 1.46 (d, 1H, J 11 Hz), 2.87 (d, 1H, J 11 Hz), 7.1–7.5 (m, 10H). Series of isotopic peaks of molecular ions with the intensity ratios corresponding to the presence of two chlorine atoms in the molecules were observed in the mass spectra of (6a,b) and (6'a,b).

Control experiments showed that the process of hydrosilylation and dichlorocarbene addition fails to occur without the appropriate catalysts. We have also examined the possibility of preparing an active hydrosilylation catalyst *in situ*. Owing to its low solubility in the reaction mixture, K_2PtCl_6 used alone fails to promote the hydrosilylation of $\text{PhC}\equiv\text{CH}$ with Et_3SiH . Introduction of stoichiometric amounts of $[\text{Et}_3\text{PhCH}_2\text{N}]\text{Cl}$ leads to a significant rise in product yield (Table 1) indicating catalyst [(3)] formation *in situ*. However, this system {a mixture of K_2PtCl_6 and $[\text{Et}_3\text{PhCH}_2\text{N}]\text{Cl}$ (1:2)} is significantly less active than the platinate (3) prepared prior to use (Table 1). This may be due to the fact that the formation of catalyst (3) under hydrosilylation conditions does not proceed quantitatively.

Thus quaternary ammonium chlorometallates proposed as bifunctional catalysts are efficient both in reactions of metal-complex and phase-transfer catalysis. Moreover, their catalytic activity in both types of reactions for the examples studied is not lower than that of the conventional catalysts, and their bifunctionality enables two types of reactions to be run consecutively in the same reaction vessel.

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