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PHASE-TRANSFER CATALYSED SUBSTITUTION OF GROUP VI METAL CARBONYLS

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Summary

The substitution of Group VI metal carbonyls by tertiary phosphines, triphenylarsine or dipyridyl is greatly accelerated by a two-phase system, benzene/50% aqueous sodium hydroxide, in the presence of tetra-n-butylammonium iodide as phase-transfer catalyst.

Discussion and results

There has been a great deal of preparative and kinetic work on the substitution of Group VI metal carbonyls by nitrogen-, phosphorus- or arsenic-donor ligands [1—3]. These carbonyls are rather inert and undergo measurable rates of substitution or carbon monoxide exchange at relatively high temperatures (110—170°C). Solvents are reported to have a minor effect on rates of substitution [1]. An important development in this area was the discovery that sodium borohydride in boiling methylated spirits catalysed the substitution and in this way many derivatives of the type $[M(CO)_{6-x}L_x]$, M = Cr, Mo or W; L = tertiary phosphine, arsine, stibine or amine, were prepared [4]. In refluxing methylated spirit sodium borohydride would solvolyse rapidly but sodium ethoxide in ethanol was found not to catalyse the substitution. We find however that sodium hydroxide in aqueous ethanol containing a little water (ca. 95% v/v) catalyses substitution of these carbonyls e.g. treatment of $[Mo(CO)_6]$ with triphenylphosphine in boiling aqueous ethanol containing sodium hydroxide (ca. 0.14 *M*) gave after 2 h reflux *cis*-$[Mo(CO)_4(PPh_3)_2]$ in 72% yield and with $Ph_2PCH_2CH_2PPh_2$(diphos) similar treatment gave $[Mo(CO)_4(diphos)]$ in 82% yield. There is a clear difference in the catalysis by sodium borohydride and by sodium hydroxide, however, since sodium borohydride causes formation of *trans*-$[Mo(CO)_4(PPh_3)_2]$ (90% yield) [4]. In the absence of sodium hydroxide the yields of substitution products are much less [4].

Since it is now established that the effectiveness of hydroxide in many organic reactions is increased to a remarkable degree by phase-transfer catalysis [5,6] we have investigated this phenomenon as a means of promoting the substitution of Group VI carbonyls. We have used as the two-phase system an organic phase, consisting of the metal carbonyl and the substituting ligand in benzene, and an aqueous phase, consisting of 50% aqueous sodium hydroxide solution with a little tetra-n-butylammonium iodide as phase-transfer catalyst. In general catalysis is very efficient, substitution occurring much faster than in the one-phase systems described above or previously [4]. Thus a mixture of $[Mo(CO)_6]$ and diphos in benzene and 50% aqueous sodium hydroxide with tetra-n-butylammonium hydroxide as catalyst gives after 4 h $[Mo(CO)_4(diphos)]$ in 87% yield (see Experimental). A selection from our other results is given in Table 1. The compounds were identified by their characteristic IR absorption spectra in the $\nu(CO)$ region [1—4]. As a preparative method it is very convenient to use. In the absence of the phase-transfer catalyst substitution does not occur or occurs to a very small extent. We feel that the phase-transfer catalysis could promote many reactions in organometallic/coordination chemistry.

Since Group VI carbonyl halides (X) of type $[M(CO_5X]^-$ and also carbene complexes $[M(CO)_5C(OR)R']$ are substituted by tertiary phosphines quite smoothly at ca. 25°C [1,2] we suggest that the function of the hydroxide ion in our systems is to give a substitution-labile species $[M(CO)_5COOH]^-$ which after substitution by the tertiary phosphine etc. loses hydroxide ion. We have also investigated the possibility that the displaced carbon monoxide is converted into sodium formate but could not detect this by IR spectroscopy.

TABLE 1

REACTANTS, PRODUCTS AND CONDITIONS[a] FOR THE SYNTHESIS OF SUBSTITUTED GROUP VI METAL CARBONYLS IN THE TWO-PHASE BENZENE/50% SODIUM HYDROXIDE SYSTEM

Substituting ligand (L)	Ratio [L]/[M] (mols)	Temp. (°C)	Reaction time (h)	Products (yield %)
Chromium				
diphos	1	80	2	$[Cr(CO)_4L]$ (63)
$AsPh_3$	2	80	2	$[Cr(CO)_5L]$ (62)
Molybdenum				
PPh_3	2	80	4	$[Mo(CO)_5L]$ (minor) *cis*-$[Mo(CO)_4L_2]$ (major)
PPh_3	2	45	2	$[Mo(CO)_5L]$ (80)
diphos	1	80	2	$[Mo(CO)_4L]$ (91)
diphos	1	55	2	$[Mo(CO)_4L]$ (94)
diphos	1	25	2	$[Mo(CO)_4L]$ (87)
dipy	1	80	4	$[Mo(CO)_4L]$ (70)
PMe_2Ph	1	80	2	$[Mo(CO)_5L]$
$AsPh_3$	1	80	2	$[Mo(CO)_5L]$ (53)
Tungsten				
diphos	1	80	2	$[W(CO)_4L)]$ (75)
diphos	1	25	2	$[W(CO)_4L]$ (51)

[a] The concentrations of reactants and methods of work-up are very similar to those described in the example.

Experimental

Melting points were determined on a Kofler hot-stage apparatus and are corrected. IR spectra were determined on a Perkin—Elmer R257 (4000—400 cm^{-1}) spectrometer. A typical preparation is given below; the reaction conditions and yields etc. for other preparations are shown in Table 1.

Tetracarbonyl{1,2-bis(diphenylphosphino)ethane}molybdenum(0)

A mixture of molybdenum hexacarbonyl (0.247 g, 0.90 mmol), 1,2-bis-(diphenylphosphino)ethane (0.368 g, 0.90 mmol), benzene (20 ml), 50% w/w aqueous sodium hydroxide solution {sodium hydroxide (2 g)/water (2 g)}, and tetra-n-butylammonium iodide (0.0224 g, 0.060 mmol) was stirred (magnetic stirrer) under nitrogen in an oil bath at 80°C for 2 h. The mixture was cooled and the product isolated from the organic layer by evaporation and addition of ethanol. The product was purified by recrystallization from dichloromethane/methanol. Yield 0.52 g (91%).

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