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Preliminary communication

ELECTROCHEMICAL PREPARATION OF d^8 ORGANOMETALLIC RHODIUM AND IRIDIUM COMPLEXES

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Summary

$M(R)(CO)(PPh_3)_2$ compounds (M = Rh, Ir; R = Me, *p*-tolyl, *p*-methoxyphenyl, C_6F_5, Ph_3C and Ph) have been prepared by oxidative addition to a d^8 halogen or a d^{10} anionic complex followed by electrochemical reduction.

We previously observed that the electrochemical reduction of d^6 rhodium and iridium hydrido dihalogen complexes is characterized by a two-electron uptake with release of the halide ligands to yield the d^8 metal hydride [1]. With closely analogous behaviour, the d^6 $M(R)Cl_2(CO)(PPh_3)_2$ complexes (M = Rh, Ir; R = alkyl or aryl ligand) have been found to be reduced in a single two-electron step to give the d^8 organometallic derivatives, $M(R)(CO)(PPh_3)_2$. These compounds are reduced at more negative potentials than the parent species so that the electrolysis at an appropriate potential of the d^6 complex results in the formation of the σ-alkyl or σ-aryl complex as the final product of the electrode reaction. Therefore this route can provide a simple and reliable route to some organometallic compounds, such as $Ir(Me)(CO)(PPh_3)_2$, which are difficult to prepare by the usual chemical methods [2, 3].

There are two steps in the method: (i) oxidative addition of the organic halide to a d^8 halogen complex; (ii) electrochemical reduction of the resulting d^6 complex. The most important restriction on the applicability of this route is the difficulty of obtaining the d^6 complexes. Thus we have devised an alternative route which gives the same organometallic derivatives, by oxidative addition to the d^{10} anionic complexes [4]. The results are summarized in Table 1.

We describe two experiments illustrative of the methods used.

Method A. The electrochemical equipment and the procedure were as

TABLE 1

EXPERIMENTAL DETAILS FOR PREPARATIVE ELECTROLYSIS

Starting compound	$E_{1/2}$[a]	Organic halide	Product	Method	ν(CO)	Reference
$\mathrm{Rh(Ph)Cl_2(CO)(PPh_3)_2}$	−1.34	......	$\mathrm{Rh(Ph)(CO)(PPh_3)_2}$	A	1969	5
$\mathrm{Rh(\mathit{p}\text{-}CH_3Ph)Cl_2(CO)(PPh_3)_2}$	−1.38	......	$\mathrm{Rh(\mathit{p}\text{-}CH_3Ph)(CO)(PPh_3)_2}$	A	1955	This work [b]
$\mathrm{Rh(\mathit{p}\text{-}ClPh)Cl_2(CO)(PPh_3)_2}$	−1.27	......	$\mathrm{Rh(\mathit{p}\text{-}ClPh)(CO)(PPh_3)_2}$	A	1960	This work [b]
$\mathrm{Rh(\mathit{p}\text{-}CH_3OPh)Cl_2(CO)(PPh_3)_2}$	−1.38	......	$\mathrm{Rh(\mathit{p}\text{-}CH_3OPh)(CO)(PPh_3)_2}$	A	1955	This work [b]
$\mathrm{RhCl(CO)(PPh_3)_2}$	−2.05	$\mathrm{CH_3I}$	$\mathrm{Rh(Me)(CO)(PPh_3)_2}$	B	1962	5
$\mathrm{RhCl(CO)(PPh_3)_2}$	−2.05	$\mathrm{C_6F_5I}$	$\mathrm{Rh(C_6F_5)(CO)(PPh_3)_2}$	B	1955	6
$\mathrm{RhCl(CO)(PPh_3)_2}$	−2.05	$\mathrm{Ph_3CBr}$	$\mathrm{Rh(Ph_3C)(CO)(PPh_3)_2}$	B	1965	This work [b]
$\mathrm{Ir(Me)ClI(CO)(PPh_3)_2}$	−1.95	......	$\mathrm{Ir(Me)(CO)(PPh_3)_2}$	A	1935	3
$\mathrm{Ir(Ph)Cl_2(CO)(PPh_3)_2}$	−1.92	......	$\mathrm{Ir(Ph)(CO)(PPh_3)_2}$	A	1939	2
$\mathrm{IrCl(CO)(PPh_3)_2}$	−2.22	$\mathrm{CH_3I}$	$\mathrm{Ir(Me)(CO)(PPh_3)_2}$	B	1935	3
$\mathrm{IrCl(CO)(PPh_3)_2}$	−2.22	$\mathrm{C_6F_5I}$	$\mathrm{Ir(C_6F_5)(CO)(PPh_3)_2}$	B	1965	6
$\mathrm{IrCl(CO)(PPh_3)_2}$	−2.22	$\mathrm{Ph_3CBr}$	$\mathrm{Ir(Ph_3C)(CO)(PPh_3)_2}$	B	1950	This work [b]

[a] Volts vs. Ag/Ag^+ 0.1 *M* CH_3CN soln. The reduction potential was chosen about 0.2 V past $E_{1/2}$. [b] KBr disk.

previously described [1]. A 3 x 10^{-3} M solution of the d^6 complex in 50% acetonitrile/50% benzene containing 0.1 M tetraethylammonium perchlorate as supporting electrolyte was electrolyzed at the appropriate potential (see Table 1) on the mercury electrode. At the end of electrolysis the dark yellow solution was evaporated under reduced pressure to a small volume. On addition of acetonitrile, the product precipitated as a yellow solid, which was filtered off, washed with acetonitrile, and dried under vacuum. All operations were carried out under argon.

This electropreparation is especially suitable for giving solutions of the organometallic compound, which are obtained in a one-step operation without any other reducing agents present.

Method B. The electrochemical procedure for the preparation of the metal carbonyl anions, $[M(CO)(PPh_3)_3]^-$, is identical with that previously described [4]. A 3 x 10^{-3} M solution of $MCl(CO)(PPh_3)_2$ in 50% acetonitrile/50% toluene which was 0.1 M in tetraethylammonium perchlorate and at the same time 10^{-2} M in PPh_3 was electrolyzed at low temperature ($\simeq -30°C$). At the end of electrolysis the stoichiometric amount of the appropriate organic halide was added. Within a few minutes a change of colour from that of the deep cherry solution to the yellow product indicated the reaction to be completed. The further steps of the preparation are identical with those described for method A.

The identity of the species obtained by electrochemical methods was checked by means of their elemental analysis and IR spectra, for known compounds these were identical with those of authentic samples [2, 3, 5, 6].

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