

Tris- and Tetra-perhalogenoaryl Metallates of Cobalt(II), Nickel(II), Palladium(II), and Platinum(II)

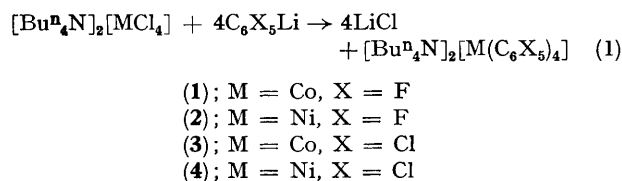
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Summary The reaction of $[\text{Bu}^n_4\text{N}]_2[\text{MCl}_4]$ ($\text{M} = \text{Co}$ or Ni) with LiC_6F_5 or LiC_6Cl_5 , and of $\text{MCl}_2(\text{tht})_2$ ($\text{M} = \text{Pd}$ or Pt , $\text{tht} = \text{tetrahydrothiophen}$) with LiC_6F_5 gives $[\text{Bu}^n_4\text{N}]_2[\text{M}(\text{C}_6\text{F}_5)_4]$ ($\text{M} = \text{Co}$, Ni , or Pd), $[\text{Bu}^n_4\text{N}]_2[\text{M}(\text{C}_6\text{Cl}_5)_4]$ ($\text{M} = \text{Co}$ or Ni), and $[\text{Bu}^n_4\text{N}]_2[\text{M}(\text{C}_6\text{F}_5)_3(\text{tht})]$ ($\text{M} = \text{Pd}$ or Pt) which, except for the cobalt derivatives, are stable towards heat, daylight, and atmospheric moisture.

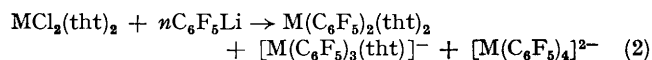
COMPOUNDS containing π -acceptor Group 5B ligands are by far the most numerous and the most stable of all alkyl and aryl derivatives of transition metals, their stability being attributed to kinetic factors. The stability of these compounds has been an obstacle in the synthesis of certain other types of compounds, since the processes come to a standstill as soon as relatively inert intermediate species are formed. Thus, the arylation of halogeno-complexes of the MX_2L_2 type ($\text{M} = \text{Group 8A metal}$, $\text{X} = \text{halogen}$, $\text{L} = \text{a } \pi\text{-acceptor Group 5B ligand}$) with a large excess of an organomagnesium or organolithium compound generally leads to the introduction of a maximum of two radicals, R, to give MR_2L_2 ; in some cases only compounds of the MXRL_2 type are obtained. The latter is believed to be due to steric reasons especially if R is a bulky or *ortho*-substituted (e.g., 2,6-dimethylphenyl¹ or pentachlorophenyl²) group.

It is, nevertheless, possible to synthesize anionic derivatives with three or even four perhalogenoaryl groups³ attached to the central atom by using starting compounds without ancillary ligands or at least without ligands of Group 5B.

Thus, the reaction of $[\text{Bu}^n_4\text{N}]_2[\text{MCl}_4]$ ($\text{M} = \text{Co}$ or Ni) with $\text{C}_6\text{X}_5\text{Li}$ ($\text{X} = \text{F}$ or Cl) (1:7) in diethyl ether (-78°C for $\text{C}_6\text{F}_5\text{Li}$; -15°C for $\text{C}_6\text{Cl}_5\text{Li}$) leads to all the possible homoleptic tetra-aryl derivatives [equation (1)]. The reaction did not take place when $\text{M} = \text{Pd}$ or Pt under

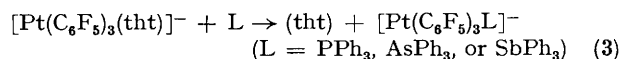


similar conditions $\{-78^\circ\text{C}$ to room temperature, using alkaline or ammonium salts of anions of the $[\text{MX}_4]^{2-}$ type ($\text{X} = \text{Cl}$, Br , or CN)}. However, in these cases the neutral adducts $\text{MCl}_2(\text{tht})_2$ ($\text{tht} = \text{tetrahydrothiophen}$) may be used as starting compounds as these react with $\text{C}_6\text{F}_5\text{Li}$ according to equation (2). When the ratio of



$\text{MCl}_2(\text{tht})_2:\text{C}_6\text{F}_5\text{Li}$ is 1:3, the neutral complexes $\text{Pd}(\text{C}_6\text{F}_5)_2(\text{tht})_2$ (5) and $\text{Pt}(\text{C}_6\text{F}_5)_2(\text{tht})_2$ (6) precipitate from ether solutions in 55 and 26% yields, respectively. Partial evaporation of the filtrate and addition of ethanol and Bu^n_4NCl results in crystals of $[\text{Bu}^n_4\text{N}][\text{Pd}(\text{C}_6\text{F}_5)_3(\text{tht})]$ (7) (12% yield) and $[\text{Bu}^n_4\text{N}][\text{Pt}(\text{C}_6\text{F}_5)_3(\text{tht})]$ (8) (56% yield), respectively. If $\text{MCl}_2(\text{tht})_2$ ($\text{M} = \text{Pd}$) and $\text{C}_6\text{F}_5\text{Li}$ are used in the ratio 1:5, the yield of (5) decreases (15%) and $[\text{Bu}^n_4\text{N}]_2[\text{Pd}(\text{C}_6\text{F}_5)_4]$ (9) (60%) can be obtained from the filtrate. In the case of $\text{M} = \text{Pt}$, however, the reaction leads to an oil which could contain the anion $[\text{Pt}(\text{C}_6\text{F}_5)_4]^{2-}$, but we were not able to obtain it in crystalline form.

In ethanol solution the neutral ligand in the anion $[\text{Pt}(\text{C}_6\text{F}_5)_3(\text{tht})]^-$ can be readily displaced by other neutral π -acceptors [equation (3)]. Thus we were able to isolate



the corresponding tetrabutylammonium salts, $[\text{Bu}^n_4\text{N}][\text{Pt}(\text{C}_6\text{F}_5)_3\text{L}]$ [$\text{L} = \text{PPh}_3$ (10), AsPh_3 (11), or SbPh_3 (12)], in good yields (75–80%).

The cobalt derivatives (1) and (3) are unstable in acetone solution and their conductivity could not be determined (*cf.* Table). Compounds (1) and (3) are also unstable in the solid state and decompose in daylight and in atmospheric moisture. All the other compounds are light- and air-stable at room temperature both as solids and in solution {*cf.* the sensitivity of $\text{Li}_2[\text{NiR}_4] \cdot x\text{THF}$ ($\text{R} = \text{Me}$, Ph ; $\text{THF} = \text{tetrahydrofuran}$) in daylight and atmospheric moisture⁴}.

TABLE. M.p.s and conductivities of complexes (1)–(12).

Complex	M.p./°C	$\Delta\text{m}/\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ^a
(1)	130 (decomp.)	Decomp. in solution
(2)	175	210
(3)	95	Decomp. in solution
(4)	167 (decomp.)	194
(5)	150 (decomp.)	0
(6)	264 (decomp.)	0
(7)	102	99
(8)	160	100
(9)	158	208
(10)	172	92
(11)	161	91
(12)	133	91

^a Measured in acetone, concentration *ca.* $5 \times 10^{-4} \text{mol l}^{-1}$.

All complexes having the C_6F_5 group show absorptions at ν *ca.* 1500, 1050, and 950cm^{-1} , whilst the presence of the C_6Cl_5 group is confirmed by bands at ν *ca.* 1315, 1305, 1280, and 660cm^{-1} . Complexes (1)–(12) gave satisfactory C, H, and N analyses.

The melting or decomposition points of the complexes, together with their conductivities are given in the Table. Their conductivities (in acetone solution) are those expected; thus (5) and (6) are non-conducting, (2), (4), and (9) are 2:1 electrolytes, whilst the others are 1:1 electrolytes.

(Received, 19th July 1977; Com. 736.)

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