A New Type of σ-Bonded Organosilver Compound: $[Ag{-}C(OR){=}NAr]_3$

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Summary Reaction of alcoholic KOH with $(ArNC)AgCl$ gives σ-bonded organosilver compounds $[Ag{-}C(OR){=}NAr]_3$, which undergo metathesis with chloro-complexes of Au^{I}, Hg^{II}, and Pt^{II} to give σ-bonded alkyl complexes of these metals.

REACTION of metal derivatives with isocyanides in alcoholic potassium hydroxide may yield zerovalent derivatives, *e.g.*[1] $Pd(CNR)_2$; this pattern of reaction is general, *e.g.*[2] $(Ph_3P)_nPt$. In other cases there is no reduction, and compounds with a metal–carbon σ-bond are obtained, *e.g.*[3] *cis*-$(Ph_3P)(p\text{-}MeC_6H_4NC)Pt[C(OMe){=}NC_6H_4Me\text{-}p)]_2$, $(Ph_3P)AuC(OR){=}NAr$,[4] or[5] $[AuC(OR){=}NC_6H_{11}]_3$.

We report a similar reaction (1) with isocyanide complexes† of silver(I). The white compounds were extracted

$$(ArNC)AgCl + ROH + KOH = KCl + H_2O + \tfrac{1}{3}[AgC(OR) = NAr]_3 \qquad (1)$$
$$(Ar = p\text{-}MeC_6H_4;\ R = Me, Et, Pr^n).$$

from the brownish precipitate with chloroform, and were precipitated by addition of the appropriate alkanol. The proposed formulae are supported by analytical, i.r. ($\nu_{C=N}$ *ca.* 1520vs; $\nu_{C=OR}$ *ca.* 1100s cm^{-1}), and n.m.r. data [R = Et; τ (saturated $CDCl_3$ solution) 8·80 (t), 5·87 (q,Et), 7·70 (s, *p*-Me), and 3·17—2·67 (complex, C_6H_4)]. The compounds are sparingly soluble, especially when R = Me, and light- and heat-sensitive. Nevertheless, when R = Pr^n, the molecular weight could be determined by cryoscopy in benzene and by osmometry in chloroform (Found: 882 and 814 resp.; $C_{33}H_{42}Ag_3N_3O_3$ requires 852), suggesting that the compounds are trimers, probably with N→Ag bonds.

This type of silver compound is one of the most stable non-fluorinated σ-bonded type of derivative of the metal yet known.[6]

These compounds are useful synthetic intermediates, as shown by the following reactions ($Y = p\text{-}MeC_6H_4N{=}C{-}OEt$):

$$(Ph_3P)AuCl + AgY = AgCl + (Ph_3P)AuY^{4}$$

$$(Ph_3P)_2HgCl_2 + 2AgY = 2(Ph_3P)AgCl + HgY_2{}^{\dagger}$$
(m.p. 133—134 °C)

$$cis\text{-}(Ph_3P)_2PtCl_2 + AgY = AgCl + (Ph_3P)_2PtClY^{\dagger}$$
(m.p. 193—195 °C)

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† Satisfactory analytical, i.r., and n.m.r. data were obtained. *E.g.*, for HgY_2, τ ($CDCl_3$) 8·72 (*t*), 5·89 (q, Et), 7·67 (s, *p*-Me), and 3·60—2·84 (complex, C_6H_4).

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