

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

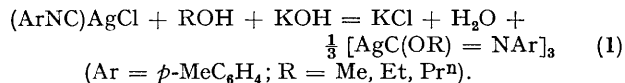
By GIOVANNI MINGHETTI, FLAVIO BONATI, and (MISS) MARIAFEDERICA MASSOBRIO

(Istituto di Chimica Generale dell'Università di Milano, Laboratorio CNR, via Venezian 21, 20133 Milano, Italy)

Summary Reaction of alcoholic KOH with $(\text{ArNC})\text{AgCl}$ gives σ -bonded organosilver compounds $[\text{Ag}-\text{C}(\text{OR})=\text{NAr}]_3$, 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 $\text{Pd}(\text{CNR})_2$; this pattern of reaction is general, *e.g.*² $(\text{Ph}_3\text{P})_n\text{Pt}$. In other cases there is no reduction, and compounds with a metal-carbon σ -bond are obtained, *e.g.*³ *cis*- $(\text{Ph}_3\text{P})(p\text{-Me-C}_6\text{H}_4\text{NC})\text{Pt}[\text{C}(\text{OMe})=\text{NC}_6\text{H}_4\text{Me-}p]_2$, $(\text{Ph}_3\text{P})\text{AuC}(\text{OR})=\text{NAr}$,⁴ or⁵ $[\text{AuC}(\text{OR})=\text{NC}_6\text{H}_{11}]_3$.

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



from the brownish precipitate with chloroform, and were precipitated by addition of the appropriate alkanol. The proposed formulae are supported by analytical, i.r. ($\nu_{\text{C}=\text{N}}$ *ca.* 1520 vs; $\nu_{\text{C}=\text{OR}}$ *ca.* 1100s cm⁻¹), and n.m.r. data [R = Et;

† Satisfactory analytical, i.r., and n.m.r. data were obtained. *E.g.*, for HgY_2 , τ (CDCl₃) 8.72 (*t*), 5.89 (*q*, Et), 7.67 (*s*, *p*-Me), and 3.60—2.84 (complex, C₆H₄).

¹ L. Malatesta, *J. Chem. Soc.*, 1955, 3924.

² L. Malatesta and C. Cariello, *J. Chem. Soc.*, 1958, 2323.

³ G. Minghetti and F. Bonati, *Rend. Accad. Naz. Lincei, Classe Sci. fis. mat. nat.*, 1970, [VIII], 59, 287.

⁴ G. Minghetti and F. Bonati, *Gazzetta*, 1972, 102, 205.

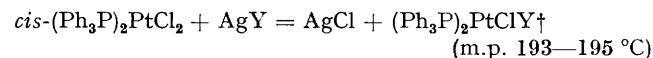
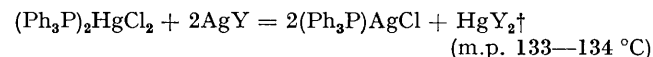
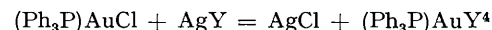
⁵ G. Minghetti and F. Bonati, *Angew. Chem.*, 1972, 84, 482; *Angew. Chem. Internat. Edn.*, 1972, 11, 429.

⁶ C. D. M. Beverwijk, G. J. M. van der Kerk, A. J. Leusink, and J. G. Noltes, *Organometallic Chem. Rev., A*, 1970, 5, 215; C. D. M. Beverwijk and G. J. M. van der Kerk, *J. Organometallic Chem.*, 1972, 43, C 11.

τ (saturated CDCl₃ solution) 8.80 (*t*), 5.87 (*q*, Et), 7.70 (*s*, *p*-Me), and 3.17—2.67 (complex, C₆H₄). The compounds are sparingly soluble, especially when R=Me, and light- and heat-sensitive. Nevertheless, when R = Prⁿ, the molecular weight could be determined by cryoscopy in benzene and by osmometry in chloroform (Found: 882 and 814 resp.; C₃₃H₄₂Ag₃N₃O₃ 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*-MeC₆H₄N=C-OEt):



(Received, 22nd December 1972; Com. 2127.)