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Preliminary communication

Complexes of the organometallic ligands $(Ph_3P)Au{-}C(OR){=}NAr$ and $[(RO)(Ar{-}N{=})C]_2Hg$

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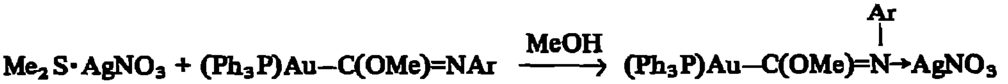
SUMMARY

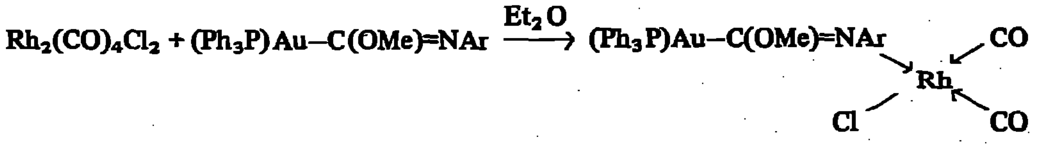
The organometallic compounds $(Ph_3P)Au{-}C(OMe){=}NAr$ and $[(EtO)(Ar{-}N{=})C]_2Hg$ can act as monodentate or as bidentate ligand, respectively, towards another, different metal atom (*e.g.* Ag and Rh).

Some complexes containing the $M{-}C(OR){=}NR'$ grouping were described recently (M = Pt [1a], Au [1,2], Ag [3], Hg [3]). Some were found to be cyclic trimers, *e.g.* $[M{-}C(OR){=}NR]_3$ (M = Au [2], Ag [3]), stable in solution and even in the gas phase (M = Au; $R = R' = CH_3$). Their stability may be due, *inter alia*, to the strength of the N→Au bond and/or to an electron delocalization over the nona-atomic ring. If the nitrogen atom of the metal-bonded organic ligand is a good donor, then the related compounds $(Ph_3P)Au{-}C(OCH_3){=}NAr$ [1] and $[(C_2H_5O)(Ar{-}N{=})C]_2Hg$ [3] ($Ar = p\text{-}CH_3C_6H_4$) should behave as monodentate and as bidentate ligand, respectively, towards another, different metal. This was shown to be correct by observation of the following reactions, which yielded the compounds (I)–(V), (satisfactory analyses, and IR, NMR and conductivity data were obtained in each case).



$$Me_2S\cdot AgNO_3 + (Ph_3P)Au{-}C(OMe){=}NAr \xrightarrow{MeOH} (Ph_3P)Au{-}C(OMe){=}\overset{\overset{\displaystyle Ar}{|}}{N}{\rightarrow}AgNO_3$$

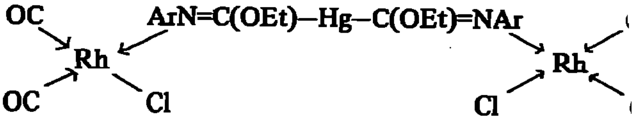
(I), $\nu(C{=}N)$ 1520 cm^{-1}



$$Rh_2(CO)_4Cl_2 + (Ph_3P)Au{-}C(OMe){=}NAr \xrightarrow{Et_2O} (Ph_3P)Au{-}C(OMe){=}NAr{\rightarrow}Rh(CO)_2Cl$$

(II), $\nu(C{=}N)$ 1515, $\nu(CO)$ 2075, 2005 cm^{-1}, yellow

$$\mathrm{Rh_2(CO)_4Cl_2 + [(EtO)(Ar{-}N{=})C]_2Hg \xrightarrow{Et_2O}}$$

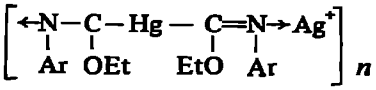


(III), ν(C=N) 1555, ν(CO) 2080, 2000 cm^{-1}, dark yel

$$\mathrm{AgClO_4 + 2\,(Ph_3P)Au{-}C(OMe){=}NAr \xrightarrow{C_6H_6} [\{(Ph_3P)Au{-}C(OMe){=}NAr\}_2Ag]^+ClO_4^-}$$

(IV), ν(C=N) 1555, ν(ClO_4^-) 1080vs, 625 cm^{-1}

$$\mathrm{AgClO_4 + [(EtO)(Ar{-}N{=})C]_2Hg \xrightarrow{C_6H_6}}$$



$$\left[\leftarrow \underset{Ar}{\mathrm{N}} - \underset{OEt}{\mathrm{C}} - \mathrm{Hg} - \underset{EtO}{\mathrm{C}} = \underset{Ar}{\mathrm{N}} \rightarrow \mathrm{Ag}^+\right]_n \quad n\mathrm{ClO_4^-}$$

(V), ν(C=N) 1580, ν(ClO_4^-) 1080 vs, 625 cm^{-1}

Compound (V) is soluble only in acetonitrile, and is likely to be a coordination polymer.

The organometallic ligand can be recovered unchanged from complex (II) by displacement with a conventional ligand, such as Ph_3P:

$$\mathrm{(II) + 2\,Ph_3P \xrightarrow{Et_2O} (Ph_3P)_2(CO)RhCl + (Ph_3P)Au{-}C(OMe){=}NAr + CO}$$

In all the compounds (I)—(V) the ν(C=N) is found at a lower frequency than in the parent ligand (1575 and 1600 cm^{-1} in the gold and mercury containing ligand resp.). In the carbonyl derivatives (II) and (III) the carbonyl stretching vibrations are in the same position as in the complexes of other nitrogen containing ligands, *e.g.* in $(CO)_2Rh(R{-}NH_2)Cl$ [4] or in $(CO)_2Rh(N{\equiv}C{-}R)Cl$ [5], suggesting that the organometallic ligands are mainly σ-donors, as expected for nitrogen ligands.

The reactions leading to compounds (I)—(V) include ligand displacement, bridge splitting and addition to a cation; they show that the gold or mercury containing compounds employed are organometallic ligands of a type previously unknown. These ligands are basic, as evidenced by the isolation of the corresponding picrates, $[(Ph_3P)Au{-}C(OMe){=}NHAr]^+(C_6H_2O_7N_3)^-$ and $[\{(EtO)(Ar{-}NH)C\}_2Hg]^{2+}2(C_6H_2O_7N_3)^-$ obtained from ether solutions.

The most closely related known ligands are imidic esters, $R{-}C({=}NR')OR''$; a few complexes of these basic molecules are known, *e.g.* [6] $ReCl_4[MeC({=}NH)OR]_2$, but they were obtained only indirectly, by reaction of $ReCl_4(MeCN)_2$ with an alcohol[6,7].

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