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Preliminary communication

BISMUTH—CARBON BOND FISSION IN THE REACTION OF PALLADIUM(II) SALTS WITH TRIS(*o*-DIMETHYLARSINOPHENYL)BISMUTHINE

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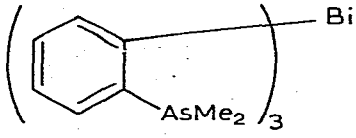
Summary

Tris(*o*-dimethylarsinophenyl)bismuthine reacts with sodium tetrachloropalladate(II) to form a palladium(II) complex of phenyldimethylarsine and elemental bismuth.

Tris(*o*-dimethylarsinophenyl)bismuthine, (Bi(*o*-$C_6H_4AsMe_2$)$_3$, bitas) reacts with nickel(II) salts to yield [Ni(bitas)X]$^+$ which contain As_3BiX donor sets [1].



(bitas)

Here we report the reaction of bitas with palladium(II) salts which might reasonably have been expected to yield species such as [Pd(bitas)X]$^+$ or [Pd(bitas)X_2] but which instead yield complexes of the $PhAsMe_2$ ligand.

When an n-butanol solution of sodium tetrachloropalladate(II) is treated successively with bitas and $NaBPh_4$ (Pd/bitas/BPh_4^- ratio 1:1:1) the orange solution formed initially almost immediately becomes orange-yellow and soon begins to deposit a fine black solid. Evaporation of the liquid, extraction with dichloromethane and crystallisation yields a yellow solid which analyses (Pd, C, H, Cl) as [Pd($PhAsMe_2$)$_3$Cl]BPh_4 (yield ~50% based on Pd). Treatment of this solid with aqueous NaCN and ether extraction yields the free ligand, identified by its mass [2] and ^{1}H NMR spectra [3] as $PhAsMe_2$. The black solid dissolves

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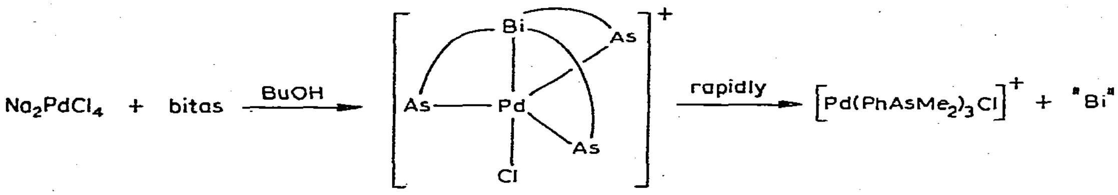
readily in dilute nitric acid and qualitative analysis of the solution indicates substantial amounts of bismuth but only traces of palladium. The black solid, which is extremely finely divided is difficult to separate by filtration and tenaciously retains organic solvents, which effectively prevents a mass balance being obtained. However, on the basis of the above evidence the reaction of bitas with Na_2PdCl_4 can be represented thus:



The mechanism of this reaction is unclear, but GLC/IR spectral examination of the solvent after the reaction indicates the presence of other organic products, including a condensed aldehyde. Thus the alcohol solvent is probably the source of hydrogen required to form $PhAsMe_2$, probably via an oxidative addition, β-elimination sequence at the palladium [4].

The nickel(II) complexes of bitas react with $PdCl_4^{2-}$ in n-BuOH or EtOH to yield black precipitates consistent with the replacement of nickel(II) by palladium(II) and subsequent ligand decomposition as above. This, incidentally, confirms that C—Bi bond fission has not occurred in the nickel complexes.

Tris(3-dimethylarsinopropyl)bismuthine appears to undergo a similar reaction with $PdCl_4^{2-}$ to yield $[Pd(Me_2AsCH_2CH_2CH_3)_3Cl]^+$.

References

1 W. Levason, C.A. McAuliffe and S.G. Murray, J. Chem. Soc. Chem. Commun., (1975) 164.
2 K. Henrick, M. Mickiewicz, N. Roberts, E. Shewchuk and S.B. Wild, Aust. J. Chem., 28 (1975) 1473.
3 R.E. Hess, C.K. Haas, B.A. Kaduk, C.D. Schaeffer and C.H. Yoder, Inorg. Chim. Acta, 5 (1971) 161.
4 See, for example, P.M. Maitlis, The Organic Chemistry of Palladium, Volume II, Chapter 2, Academic Press, New York, 1971, and refs. therein.