Carbon Monoxide Insertion into Tin-containing Palladium and Platinum Complexes

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Summary The preparation of anionic and neutral palladium and platinum complexes, in which both carbon monoxide and the trichlorotin group are present, is discussed.

CATIONIC carbonyl complexes of palladium and platinum of the type $[M(CO)(PR_3)Cl]^+$ ($M = Pt$, $R = Et$, Ph; $M = Pd$, $R = Ph$) have been synthesised by the insertion of carbon monoxide into $[Pt(PEt_3)Cl_2]$,[1] or by bridge splitting in $[M(PPh_3)_2Cl]_2^{2+}$,[2] while the anionic hydridocarbonyl species, $[Pd(CO)HCl_2]^-$, is obtained by direct carbonylation of palladium(II) chloride in an acidified alcohol medium.[3] Palladium[4,5] and platinum[6,7] compounds containing the trichlorotin group are well known, but no complexes in which both carbon monoxide and the $SnCl_3$ group are co-ordinated to the central transition metal have been reported. The preparation of complexes of this latter type is now described.

When a refluxing methanol solution of Na_2PtCl_6 (1 mole) and $SnCl_2$ (2 moles), in which $[Pt(SnCl_3)_2Cl_2]^{2-}$ is present,[6] is treated with carbon monoxide at 1 atm. pressure, the initial light red colour of the solution slowly becomes more intense; reaction times of 1 hr. are necessary to ensure complete carbonylation. Addition of a methanol solution of NEt_4Cl (1 mole), precipitated the dark red complex $[NEt_4][Pt(CO)(SnCl_3)_2Cl]$. This formulation is supported by analytical, conductivity [molar conductance (μ) in 10^{-3}M-nitromethane solution is 84 $ohm^{-1}\,cm^2\,mole^{-1}$], and spectral data [$\nu_{CO} = 2058$ and 2033 (sh) cm^{-1}].

An identical colour change is observed when the solvent is ethanol. The tetraphenylarsonium salt isolated from this solution is the mono-solvated species, $[AsPh_4][Pt(CO)(SnCl_3)_2Cl(EtOH)]$; $\mu = 66$ $ohm^{-1}\,cm^2\,mole^{-1}$ and $\nu_{CO} = 2060$ cm^{-1}. I.r. bands at 3400 cm^{-1} (O–H), 2980, 2935, and 2880 cm^{-1} (C–H), and 1020 cm^{-1} (C–O) support the presence of solvent, while lowering of the C–O absorption from that of the free species (1086 and 1047 cm^{-1}) suggests that the ethanol is co-ordinated.

Carbonylation of the palladium–tin complex proceeds in a similar manner. Thus treatment, at the ambient temperature, of an acidified methanol solution containing $PdCl_2$ and $SnCl_2$ (mole ratio 1:10) with carbon monoxide for 20 min., gave a light red solution. Following the addition of a methanol solution of NEt_4Cl (1 mole), a small quantity of the orange complex, $[NEt_4][Pd(CO)(SnCl_3)_2Cl]$, separated on standing. For this complex, $\mu = 80$ $ohm^{-1}\,cm^2\,mole^{-1}$ and $\nu_{CO} = 2054$ cm^{-1}.

Several *in situ* reactions of these carbonyl solutions have been carried out. Reaction of the platinum solution with triphenylphosphine (PPh_3) affords the complex $[Pt(CO)(PPh_3)_2(SnCl_3)_2]$ ($\nu_{CO} = 2050$ cm^{-1}; $\mu = 24$ $ohm^{-1}\,cm^2\,mole^{-1}$) and with 1,10-phenanthroline (phen) $[Pt(CO)(phen)(SnCl_3)_2]$ ($\nu_{CO} = 2046$ cm^{-1}; $\mu = 15$ $ohm^{-1}\,cm^2\,mole^{-1}$), whilst with pyridine (py), $[Pt(CO)(py)(SnCl_3)_2]$ ($\nu_{CO} = 2041$ cm^{-1}) is obtained. Although both the phosphine and phenanthroline complexes appear to be five-co-ordinate, they are somewhat dissociated in nitromethane solution. However, poor solubility prevented determination of their molecular weights. The pyridine derivative which is insoluble in the usual organic solvents, is probably a four-co-ordinate monomer.

Similar *in situ* reactions on the palladium solution failed to yield the analogous neutral complexes. Indeed, with triphenylphosphine both carbonyl and trichlorotin groups are replaced, and the only product isolated is $[Pd(PPh_3)_2Cl_2]$. The insolubility of this species may give rise to its preferential formation over any carbonyl or metal–tin derivatives.

Satisfactory analytical data were obtained for all complexes reported. All the platinum–tin complexes gave a positive cacotheline test[8] (palladium interferes with this test).

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[1] M. J. Church and M. J. Mays, *Chem. Comm.*, 1968, 435.
[2] H. C. Clark, K. R. Dixon, and W. J. Jacobs, *Chem. Comm.*, 1968, 93.
[3] J. V. Kingston and G. R. Scollary, *Chem. Comm.*, 1969, 455.
[4] M. A. Khattak and R. J. Magee, *Chem. Comm.*, 1965, 400.
[5] G. E. Batley and J. C. Ballar, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 577.
[6] J. F. Young, R. D. Gillard, and G. Wilkinson, *J. Chem. Soc.*, 1964, 5176.
[7] R. D. Cramer, E. L. Jenner, R. V. Lindsey, and U. G. Stolberg, *J. Amer. Chem. Soc.*, 1963, **85**, 1691.
[8] A. I. Vogel, "A Textbook of Macro and Semimicro Qualitative Inorganic Analysis," 4th edn., p. 252, Longmans, London, 1954