

The Synthesis and Reactivity of Isocyanide Compounds of Zerovalent Platinum

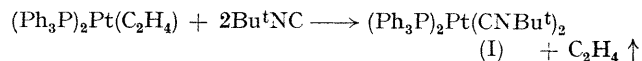
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Summary The zerovalent platinum compounds containing isocyanide, $(\text{Ph}_3\text{P})_2\text{Pt}(\text{CNBu}^t)_2$ and $(\text{Ph}_3\text{P})_2\text{Pt}(\text{CNBu}^t)(\text{CO})$, have been characterised, the former undergoing oxidative addition reactions to yield cationic species of the type $(\text{Ph}_3\text{P})_2(\text{Bu}^t\text{NC})_2\text{PtR}^+$.

SEVERAL types of ligands (phosphines, arsines, carbon monoxide, alkenes, and alkynes) are capable of stabilising platinum in a low valence state, but relatively few compounds containing such ligands have been reported.^{1,2} We have now prepared a new class of zerovalent platinum compounds using isocyanide (RNC) as the ligand species. Very recently a Pt^0 compound containing an isocyanide ligand, $(\text{PF}_3)_3\text{Pt}(\text{CNC}_6\text{H}_{11})$, has been isolated in the course of a kinetic study.³ Recent studies on related compounds of zerovalent nickel⁴ and bivalent platinum⁵⁻⁷ have shown that unique properties result from the presence of the RNC ligand.

The addition of t-butyl isocyanide to a stirred suspension of bis(triphenylphosphine)(ethylene) platinum in dry n-pentane at -20° under nitrogen results in the rapid, and

quantitative, evolution of the olefin and the formation of the isocyanide compound:



The compound is precipitated from the solution, and is obtained in high yield as a yellow solid which slowly decomposes in air but is stable under dry nitrogen. The (NC) stretching mode occurs at 2030 cm^{-1} , a lowering of 100 cm^{-1} from that of the free isocyanide, indicating appreciable back-donation from the metal to the ligand.

Treatment of the solid $(\text{Ph}_3\text{P})_2\text{Pt}(\text{CNBu}^t)_2$ with carbon monoxide (*ca.* 25 atm.) and subsequent washing with hexane yields the carbonyl, $(\text{Ph}_3\text{P})_2\text{Pt}(\text{CNBu}^t)(\text{CO})$, as a pale yellow solid. In this platinum(0) compound the (NC) stretching mode [$\nu(\text{NC})$, 2110; $\nu(\text{CO})$, 1910 cm^{-1}] is considerably higher than the bis-isocyanide compound, suggesting that carbon monoxide is a much more effective π -acceptor ligand than the isoelectronic isocyanide. Previous reports of mixed neutral ligand-isocyanide complexes

of platinum have been confined to the cationic platinum(II) species, *e.g.*, *trans*-PtH(CNBut)(PEt₃)₂⁺.⁸

The addition of one mole of reagents such as I₂, CH₃I, CF₃I, and Ph₃SnCl to a benzene solution of one mole of (I) at ambient temperatures yields products of the general formula (Ph₃P)₂Pt(CNBut)₂XY. The compounds all exhibit values of the (NC) frequency (2225—2190 cm⁻¹) higher than that of the free isocyanide, and typical of isocyanides bonded to platinum(II). The addition products obtained from I₂, CH₃I, and CF₃I show conductances in nitromethane representative of 1:1 electrolytes and may be formulated as [(Ph₃P)₂Pt(CNBut)₂R]⁺I⁻, where R = I, CH₃, or CF₃. The compound with Ph₃SnCl exhibited a lower conductivity, and in this case the precise formulation cannot be expressed unambiguously.

Similar platinum(II) species such as [(Ph₃P)₂Pt-

(CNMe)₂I]⁺I⁻ have been obtained recently from the action of methyl isocyanide on (Ph₃P)₂PtI₂ in benzene.⁵ We find that the use of *t*-butyl isocyanide in such a reaction yields a product which is identical with that obtained above from the oxidative addition reaction.

Attempts to obtain a five-co-ordinate platinum(II) compound by the alkylation of the cyanide (Ph₃P)₂Pt(CN)₂ with methyl iodide were not successful. At the temperature required to achieve alkylation (80—100°) two moles of phosphine were eliminated and the di-iodide (MeNC)₂PtI₂ was obtained.

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