The Synthesis and Reactivity of Isocyanide Compounds of Zerovalent Platinum

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Summary The zerovalent platinum compounds containing isocyanide, $(Ph_3P)_2Pt(CNBu^t)_2$ and $(Ph_3P)_2Pt(CNBu^t)(CO)$, have been characterised, the former undergoing oxidative addition reactions to yield cationic species of the type $(Ph_3P)_2(Bu^tNC)_2PtR^+$.

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, $(PF_3)_3Pt(CNC_6H_{11})$, has been isolated in the course of a kinetic study.[3] Recent studies on related compounds of zerovalent nickel[4] and bivalent platinum[5-7] 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:

$$(Ph_3P)_2Pt(C_2H_4) + 2Bu^tNC \longrightarrow \underset{(I)}{(Ph_3P)_2Pt(CNBu^t)_2} + C_2H_4\uparrow$$

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 $(Ph_3P)_2Pt(CNBu^t)_2$ with carbon monoxide (*ca.* 25 atm.) and subsequent washing with hexane yields the carbonyl, $(Ph_3P)_2Pt(CNBu^t)(CO)$, as a pale yellow solid. In this platinum(0) compound the (NC) stretching mode [ν(NC), 2110; ν(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*-$PtH(CNBu^t)(PEt_3)_2^+$.[8]

The addition of one mole of reagents such as I_2, CH_3I, CF_3I, and Ph_3SnCl to a benzene solution of one mole of (I) at ambient temperatures yields products of the general formula $(Ph_3P)_2Pt(CNBu^t)_2XY$. 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 I_2, CH_3I, and CF_3I show conductances in nitromethane representative of 1 : 1 electrolytes and may be formulated as $[(Ph_3P)_2Pt(CNBu^t)_2R]^+I^-$, where R = I, CH_3, or CF_3. The compound with Ph_3SnCl exhibited a lower conductivity, and in this case the precise formulation cannot be expressed unambiguously.

Similar platinum(II) species such as $[(Ph_3P)_2Pt(CNMe)_2I]^+I^-$ have been obtained recently from the action of methyl isocyanide on $(Ph_3P)_2PtI_2$ 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 $(Ph_3P)_2Pt(CN)_2$ 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 $(MeNC)_2PtI_2$ was obtained.

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[1] R. Ugo, *Co-ordination Chem. Rev.*, 1968, **3**, 319, and references therein.
[2] J. Chatt and P. Chini, *J. Chem. Soc.* (*A*), 1970, 1538.
[3] R. D. Johnston, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, 1971, **10**, 247.
[4] A. Greco, M. Green, S. K. Shakshooki, and F. G. A. Stone, *Chem. Comm.*, 1970, 1374.
[5] P. M. Treichel and R. W. Hess, *Chem. Comm.*, 1970, 1626.
[6] W. J. Knebel and P. M. Treichel, *Chem. Comm.*, 1971, 516.
[7] E. M. Badley, J. Chatt, and R. L. Richards, *J. Chem. Soc.* (*A*), 1971, 21.
[8] M. J. Church and M. J. Mays, *Chem. Comm.*, 1970, 1626.