Nucleophilic Additions to Isocyanide–Platinum(II) Complexes. Synthesis of $[(R_3P)_2Pt(CNMe)L]^{n+}$ Derivatives

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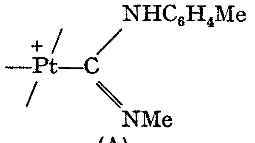
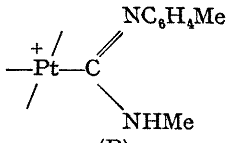
Summary The nucleophilic addition of OH^- to *trans*-$\{(Ph_3P)_2Pt(CNMe)_2\}^{2+}2BF_4^-$ gives the complex *trans*-$\{(Ph_3P)_2Pt(CNMe)[C(O)NHMe]\}^+$ which, upon treatment with HBF_4 provides a synthetic route to $\{(Ph_3P)_2Pt(CNMe)L\}^{n+}$ derivatives; SH^- and NHR^- react similarly with $\{(Ph_3P)_2Pt(CNMe)_2\}^{2+}$ to give $\{(Ph_3P)_2Pt(CNMe)[C(S)NHMe]\}^+$ and $\{(Ph_3P)_2Pt(CNMe)[C(NR)NHMe]\}^+$, respectively.

SYNTHESIS of transition-metal carboxamido-complexes has been accomplished by one of two principal methods: (1) reaction of alkylcarbamoyl chloride with metal carbonyl anions,[1] and (2) reaction of metal carbonyl derivatives (*e.g.*, cations) with primary or secondary aliphatic amines.[2,3] We report a new route to the preparation of metal carboxamido-complexes by the direct conversion of a co-ordinated isocyanide ligand into a carbamoyl ligand. The reaction of *trans*-$\{(Ph_3P)_2Pt(CNMe)_2\}^{2+}2BF_4^-$, (I), with a slight excess of hydroxide ion in acetonitrile–water, 25°, gives *trans*-$\{(Ph_3P)_2Pt(CNMe)[C(O)NHMe]\}^+$, (II) (pale yellow crystals; m.p. 183—185° dec; 95%).† This complex shows appropriate i.r. and n.m.r. properties. A possible mechanism of formation involves initial attack at the carbon atom of the co-ordinated isocyanide ligand with formation of an intermediate (enol tautomer) which rapidly rearranges to a carboxamido-structure (keto-tautomer).

We observed that hydrogen sulphide and amide ions exhibit similar nucleophilic behaviour toward (I) in polar media. Using similar conditions, SH^- gives *trans*-$\{(Ph_3P)_2Pt(CNMe)[C(S)NHMe]\}^+$, (III) (yellow needles; m.p. 117—118°; 76%), the n.m.r. and i.r. properties of which are in agreement with the structure assigned. The reaction of (I) with a slight excess of sodium *p*-toluidide in tetrahydrofuran at 25° gives $\{(Ph_3P)_2Pt(CNMe)[C(NC_6H_4Me)NHMe]\}^+BF_4^-$, (IV) (pale yellow crystals; m.p. 200—201°; 76%). Two tautomeric forms of the ligand (A) and (B), could exist; we are unable to tell by spectral data whether one or both are present, and whether they interconvert rapidly or not. Further studies may provide information on this question.



(A)



(B)

Complex (II), on treatment with fluoroboric acid (48—50%) in acetonitrile–water, rapidly evolves carbon monoxide (identified by mass spectroscopy). Upon work-up, $\{(Ph_3P)_2Pt(CNMe)(NCMe)\}^{2+}2BF_4^-$, (V), is isolated. This compound is presumably formed *via* the intermediate $\{(Ph_3P)_2Pt(CNMe)(CO)\}^{2+}$. This complex is a linkage isomer of (I). Other nitrile complexes may be prepared by appropriate choice of solvent. The nitrile ligand is particularly labile in these complexes, and is readily displaced by various neutral ligands (CH_3NC, Ph_3P, py, Me_2S, Me_3N) to give derivatives $\{(Ph_3P)_2Pt(CNMe)L\}^{2+}$ and by anions (Cl^-, I^-, N_3^-, CN^-) to give $\{(Ph_3P)_2Pt(CNMe)X\}^+$ species.

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† Satisfactory elemental analyses have been obtained for al lnew compounds reported here.

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