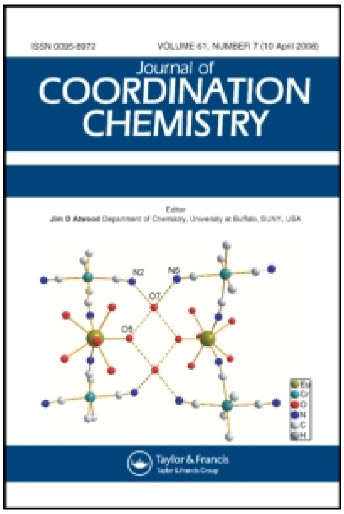

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FIVE COORDINATE PLATINUM (II) ISOCYANIDE COMPLEXES

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We have described[1] isocyanide complexes of platinum(II) having the stoichiometry $[PtX(CNCH_3)_2(PPh_3)_2]Y$*($X$ = Br,I; $Y = BF_4$, I), which are formed either from halide addition to $[Pt(CNCH_3)_2(PPh_3)_2](BF_4)_2$ or from methyl isocyanide addition to $PtX_2(PPh_3)_2$. Several analogous complexes $[Pt(R)(CNBu^t)_2(PPh_3)_2]X$ were recently reported[2] from oxidative addition reactions of $Pt(CNBu^t)_2(PPh_3)_2$. The proposed five-coordinate formulation in each instance was established by conductivity measurements on these species in acetonitrile.

One realizes, of course, that five-coordination in platinum (II) is something of a rarity, being previously restricted to several trichlorostannato-complexes,[3] and to a number of complexes involving polydentate ligands,[4] primarily phosphines and arsines. The isolation of these complexes suggests that isocyanides may also be capable of stabilization of five-coordinate species, however, and with our current interest in isocyanide complexes, we initiated further study on this subject. This work is communicated herein.

We have prepared a series of stable complexes, $[PtI(CNCH_3)_2(PR_3)_2]BF_4$, $PR_3 = PPh_3$, Ph_2PMe, $PhPMe_2$, PEt_3, in reactions of the appropriate $[Pt(CNCH_3)_2(PR_3)_2](BF_4)_2$ with tetra-*n*-butylammonium iodide in dichloromethane (25°). Stoichiometries were ascertained by analyses and by proton nmr peak intensities. Except for the triethylphosphine complex which is anomalous, these compounds are bright yellow crystalline solids, and are soluble in polar solvents giving conductivities appropriate for 1:1 electrolytes. None of these complexes lose isocyanide on mild heating in vacuum or on recrystallization. The nearly colorless complex $[PtI(CNCH_3)_2(PEt_3)_2]BF_4$ has a conductivity between the values expected for a 1:1 and 1:2 electrolyte ($\Lambda^0_M = 218$ ohm^{-1} cm^2 mol^{-1}, for a 2×10^{-4}m solution in acetonitrile), sugggesting that the iodide ion has partially dissociated from the coordination sphere.

Reactions of $[Pt(CNCH_3)_2(PPh_3)_2](BF_4)_2$ and other nucleophilic anions (Br^-, CN^-, SCN^-) yielded initially yellow solids. Only in the case of $[PtBr(CNCH_3)_2(PPh_3)_2]$ BF_4 could the five-coordinate stoichiometry be confirmed by analyses; in the other cases between one and two moles of isocyanide per mole of platinum was retained. Furthermore, all of these complexes lost methyl isocyanide on several recrystallizations (followed by decreasing intensities of methyl *vs.* phenyl protons in the nmr) giving eventually colorless $[PtX(CNCH_3)(PPh_3)_2]BF_4$. It is apparent that these complexes and methyl isocyanide exist in equilibrium in solution.

$$[PtX(CNCH_3)(PPh_3)_2]BF_4 + CH_3NC \rightleftharpoons [PtX(CNCH_3)_2(PPh_3)_2]BF_4$$

The yellow color of the five-coordinate species is useful for their qualitative identification. It arises from a new absorption at a wavelength higher than that observed in the four-coordinate complex. For example this absorption maximum for $[PtBr(CNCH_3)_2(PPh_3)_2]BF_4$ is at 315 nm ($\epsilon = 8.8 \times 10^3$ cm^{-1} M^{-1}). Absorption measurements of solutions with varying reactant concentrations (Table I) allow calculation of an equilibrium constant for the above reaction of $(9.7 \pm 3.0) \times 10^1$ M^{-1}, a value in accord with the instability of the five-coordinate species.

When iodide or bromide ion is added to $[Pt(CNCH_3)_4]$ $(BF_4)_2$, or when methyl isocyanide is added to $PtI_2(CNCH_3)_2$ or $PtBr_2(CHCH_3)_2$, bright yellow solids are obtained. Analyses on the initial products from these reactions indicate stoichiometries

* Standard abbreviations are used: Ph = phenyl, Bu^t = t-butyl, Et = ethyl, Me = methyl.

TABLE I

Determination of Equilibrium for the System

$$[PtBr(CNCH_3)(PPh_3)_2]^+ + CH_3NC \underset{CH_2Cl_2}{\overset{24^\circ}{\rightleftharpoons}} [PtBr(CNCH_3)_2(PPh_3)_2]^+$$

$$\text{where } K_{eq} = \frac{[PtBr(CNCH_3)_2(PPh_3)_2]^+}{[PtBr(CNCH_3)(PPh_3)_2]^+ [CH_3NC]}$$

A_{XY}	C_{XY} M	C_X, M	C_Y, M	K_{eq}, M^{-1}
0.494	5.6×10^{-5}	6×10^{-6}	1.0×10^{-1}	9.3×10^{1}
0.420	4.8×10^{-5}	1.4×10^{-5}	4.0×10^{-2}	8.6×10^{1}
0.380	4.3×10^{-5}	1.9×10^{-5}	2.5×10^{-2}	9.0×10^{1}
0.280	3.2×10^{-5}	3.0×10^{-5}	1.1×10^{-2}	9.7×10^{1}
0.270	3.1×10^{-5}	3.1×10^{-5}	8.5×10^{-3}	1.2×10^{2}

$K_{eq(avg.)} = 9.7 \times 10^{1}\ M^{-1}$

$XY = [PtBr(CNCH_3)_2(PPh_3)_2]^+$
$X = [PtBr(CNCH_3)(PPh_3)_2]^+$
$Y = CH_3NC$

$[PtI(CNCH_3)_{3.8}]BF_4$ $[PtI(CNCH_3)_{3.6}]I$, $[PtBr(CNCH_3)_{3.5}]BF_4$, and $[PtBr(CNCH_3)_{3.5}]Br$. The non-integral stoichiometry presumably indicates a mixture of $[PtX(CNCH_3)_4]Y$ and $[PtX(CNCH_3)_3]Y$. Each species on recrystallization loses methyl isocyanide to give analytically pure $[PtX(CNCH_3)_3]Y$ (Y = hal., BF_4); the halide salts further revert to $PtX_2(CNCH_3)_2$ on continued purification.

The equilibrium constant for the reaction:

$$[PtI(CNCH_3)_3]BF_4 + CH_3NC \rightleftharpoons [PtI(CNCH_3)_4]BF_4$$

was determined in dichloromethane, 24°, in the manner described above, using the absorption of the complex $[PtI(CNCH_3)_4]BF_4$ at 350 nm ($\epsilon = 5.6 \times 10^3\ cm^{-1}\ M^{-1}$); its value was: $1.2 \pm 0.1) \times 10^2\ M^{-1}$.

$[PtI(CNCH_3)_2(PPh_3)]PF_6$, prepared by an established procedure[5], gives the unstable adduct $[PtI(CNCH_3)_3(Ph_3P)]\ PF_6$:λ = 350 nm, $\epsilon = 1.1 \times 10^4 cm^{-1} M^{-1}; K_{eq} = (1.5 \pm 0.7) \times 10^1\ M^{-1})$ in dichloromethane, 24°, for the equilibrium

$$[PtI(CNCH_3)_2PPh_3]PF_6 + CH_3NC \rightleftharpoons [PtI(CNCH_3)_3PPh_3]PF_{.6}$$

Yellow solution indicative of five-coordination were observed in reactions of $[PtI(CNCH_3)PPh_3)_2]BF_4$ with several anions (I^-, SCN^-, CN^-) but a product was not isolated on addition of CO or Ph_3P. Five-coordination was not observed in reactions of $[Pt(CNCH_3)_4](BF_4)_2$ or $[Pt(CNCH_3)_2\ PPh_3)_2](BF_4)_2$ with chloride ion, or in the reaction of $[Pt(CNCH_3)(PPh_3)_3](BF_4)_2$ with iodide ion.

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REFERENCES

1. P. M. Treichel, W. J. Knebel, and R. W. Hess, *J. Amer. Chem. Soc.* **93**, 5724 (1971).
2. G. A. Larkin, R. Mason and M. G. H. Wallbridge, *J. Chem. Soc.* (D), 1054 (1971).
3. R. D. Cramer, R. V. Lindsay Jr., C. T. Prewitt, and U. G. Stolberg, *J. Amer. Chem. Soc.* **85**, 658 (1965).
4. J. A. Brewster, C. A. Savage, and L. M. Venanzi, *J. Chem. Soc.* 3699 (1961).
5. M. J. Church and M. J. Mays, *J. Chem. Soc.* (A), 3074, 1968.