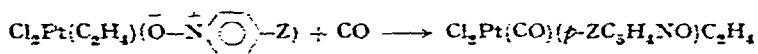


PRELIMINARY NOTES

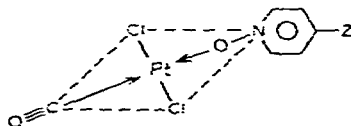
Pyridine *N*-oxide-carbonyl-dichloroplatinum(II) complexes

Previous work in this laboratory¹ has shown that the ethylene in ethylene-pyridine *N*-oxide-platinum(II) complexes is readily exchanged with other olefins. We now wish to report that carbon monoxide reacts rapidly at room conditions with solutions of these Pt(II) complexes to replace the ethylene ligand with carbon monoxide:



This reaction provides a new and simple route to platinum carbonyls. Apparently ethylene can not be displaced from 1,3-bis(ethylene)-2,4-dichloro- μ,μ' -dichlorodiplatinum(II) with carbon monoxide². However, basic organic ligands such as aniline and *p*-toluidine have been reported to react with 1,3-bis(carbonyl)-2,4-dichloro- μ,μ' -dichlorodiplatinum(II) to give similar carbonyl compounds³. The new compounds, obtained in approximately 80% yield, are characterized in Table I.

TABLE I

ANALYSIS AND PROPERTIES^a OF

Z	M.p. (dec.), °C	Calcd., %			Found ^b , %			$\nu_{\text{C-O}}$ cm ⁻¹
		C	H	Pt	C	H	Pt	
H	151-153	18.51	1.29	—	18.67	1.32	—	2105
CH ₃	155-157	20.82	1.73	—	20.70	1.59	—	2100
OCH ₃	149-151	20.05	1.67	46.6	20.00	1.54	46.7	2110
NO ₂	190-191	16.59	0.92	44.8	16.74	0.75	44.0	2134

^a Tentatively assigned *trans* configuration. ^b Analysis performed by Galbraith Laboratories, Knoxville, Tenn.

The compounds were prepared by passing a stream of carbon monoxide over a stirred solution of the appropriate ethylene *N*-oxide complex^{1,4} (1 mmole) in dry chloroform (30 ml). After several minutes, the color of the solution changed from an original bright yellow to a final pale, greenish-yellow. At this point, hexane (10 ml) was added and the solution was concentrated to induce precipitation. The compounds were recrystallized from chloroform/hexane/ether. The carbonyls were pale, greenish-yellow compounds which decomposed very rapidly when treated with water.

All the compounds gave a single, very strong carbonyl absorption in the infrared as well as characteristic pyridine *N*-oxide ligand absorptions. As further evidence for the presence of only one carbonyl group, treatment of 1.0 mmole of the pyridine

N-oxide-carbonyl-PtCl₂ complex with an excess of triphenylphosphine in a gasometric apparatus liberated 1.0 mmole of gas, and the derivative which formed contained no carbon monoxide (infrared).

Since displacement of ethylene by higher olefins in the 1-(4-*Z*-pyridine *N*-oxide)-3-ethylene-2,4-dichloroplatinum(II) complexes leads to *trans* compounds, it is reasonable to assume that carbon monoxide is also *trans* to the pyridine *N*-oxide. However, this is by no means certain. Investigations are currently underway to establish definite configuration of the complexes as well as to evaluate further applications of this synthetic route.

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An unusual adduct from 2,2'-bipyridine and diphenyltin diisocyanate

In an investigation of some organotin isocyanates it was found that diphenyltin diisocyanate was hydrolysed rapidly in the atmosphere and attempts to isolate the pure compound yielded various hydrolysis products including Ph₂Sn₂(NCO)₂O, m.p. 158-162°, and Ph₂Sn₂(NCO)(OH)O, m.p. 300-301°. These compounds are analogous to the hydrolysis products of the organotin dihalides¹.

Since complex formation can confer stability to hydrolysis, the crude diphenyltin diisocyanate was treated with 2,2'-bipyridine to give a stable adduct, m.p. 204-206° decomp., which was found from repeated analysis to have the composition bipy·[Ph₂Sn(NCO)₂]₂. (Found: C, 52.9; H, 3.6; N, 9.7; Sn, 27.0. C₃₈H₂₈O₄N₆Sn₂ calcd.: C, 52.5; H, 3.2; N, 9.7; Sn, 27.3%.) This compound contrasts with the adducts reported by Alleston and Davies², which were all shown to be of the type bipy·R₂SnX₂.

The ultra-violet absorption spectrum in dioxane indicated that the complex was dissociated into bipyridine and diphenyltin diisocyanate. The bipyridine band³ at 284 mμ showed no splitting and was in the same position as that shown by the free base in dioxane; bipy·Ph₂SnBr₂ showed identical behaviour. Okawara⁴ has recently shown that bipy·Bu₂SnCl₂ is dissociated in a number of solvents. Since dioxane is the only solvent in which the diisocyanate complex has appreciable solubility, this dissociation precluded molecular weight measurements.

The adduct can be formulated with either bridging bipyridine groups, or bridging isocyanate groups; the latter possibility seems unlikely since the NCO asymmetric