CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
WISCONSIN STATE UNIVERSITY, LA CROSSE, WISCONSIN, AND THE UNIVERSITY OF IOWA, IOWA CITY, IOWA

Reactions of Isomeric *cis*-Bis(tolyl)bis(pyridine)platinum(II) Compounds with Some Organoiodides

BY C. R. KISTNER,[1] D. A. DREW, J. R. DOYLE, AND G. W. RAUSCH

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The reactions of some organoiodides with isomeric *cis*-bis(tolyl)bis(pyridine)platinum(II) were investigated. In all of the reactions at least one tolyl group was displaced and this displacement was usually accompanied by an addition of the organoiodide resulting in a platinum(IV) compound. The reaction of allyl iodide with either the *o*-tolyl or *p*-tolyl derivative produced the identical compound $(C_5H_5N)_2Pt(C_3H_5)_2(I_3)_2$, apparently a six-coordinated platinum(IV) complex. The ultraviolet spectrum of this compound indicates the presence of the triiodide ion and the nmr spectrum of the allyl group favors a σ-bonded configuration.

The reactions of methyl iodide with platinum(II) compounds containing coordinately bound ligands such as triphenylphosphine, pyridine, and 1,5-cyclooctadiene, and σ-bound groups such as methyl or *o*-tolyl have been previously reported.[2,3] In the present study we have extended this investigation to include the reactions of the isomeric *cis*-bis(tolyl)bis(pyridine)platinum(II) compounds with ethyl iodide, propyl iodide, allyl iodide, and iodobenzene.

Experimental Section

Synthetic Procedures.—The *o*-tolyl and *p*-tolyl derivatives of the type *cis*-$(C_5H_5N)_2Pt(C_6H_4CH_3)_2$ were prepared by previously described procedures.[3]

The reactions of the organoiodides and the *o*-tolyl and *p*-tolyl derivatives were carried out according to the following procedure. A 0.3-g (0.561-mmole) sample of the tolyl derivative was mixed with 7.0 ml of the organoiodide in a heavy-walled glass tube equipped with a constriction at the top of the tube. The tube was sealed off and stored for 6 days at the temperature shown in Table I. The product was isolated by filtration and the solid crystalline residue was washed with methylene chloride. The low solubility of the products prevented effective recrystallization and the analyses reported in Table I are for the *as isolated* product. The yields ranged from 60 to 80% of the theoretical amounts.

Physical Measurements.—The infrared spectra of the products were observed over the range 700–4000 cm^{-1} in potassium bromide pressed disks and mineral oil mulls.

The proton nmr spectra were observed with a Varian A-60 instrument equipped with a Varian time-averaging computer. The samples were dissolved in deuterated dimethyl sulfoxide or tetramethylene sulfone (sulfolane). Tetramethylsilane was used as an internal standard.

The ultraviolet spectral data reported were obtained from 10^{-5} *M* solutions in ethylene chloride.

Results and Discussion

The synthetic results are summarized in the following series of equations. In all of the reactions examined at least one of the tolyl groups was displaced by the organoiodide and the displacement reaction was accompanied by an addition reaction in the examples involving allyl or alkyl iodides.

$$(C_5H_5N)_2Pt(o\text{-}CH_3C_6H_4)_2 + C_2H_5I \longrightarrow (C_5H_5N)_2Pt(o\text{-}CH_3C_6H_4)(C_2H_5)I_2$$

$$(C_5H_5N)_2Pt(p\text{-}CH_3C_6H_4)_2 + C_2H_5I \longrightarrow (C_5H_5N)_2Pt(p\text{-}CH_3C_6H_4)(C_2H_5)I_2$$

$$(C_5H_5N)_2Pt(o\text{-}CH_3C_6H_4)_2 + C_3H_7I \longrightarrow (C_5H_5N)_2Pt(o\text{-}CH_3C_6H_4)(C_3H_7)I_2$$

$$(C_5H_5N)_2Pt(o\text{-}CH_3C_6H_4)_2 + C_3H_5I \longrightarrow (C_5H_5N)_2Pt(C_3H_5)_2(I_3)_2$$

$$(C_5H_5N)_2Pt(p\text{-}CH_3C_6H_4)_2 + C_3H_5I \longrightarrow (C_5H_5N)_2Pt(C_3H_5)_2(I_3)_2$$

$$(C_5H_5N)_2Pt(o\text{-}CH_3C_6H_4)_2 + C_6H_5I \longrightarrow (C_5H_5N)_2Pt(o\text{-}CH_3C_6H_4)I$$

The reactions involving allyl iodide are of special interest in view of the ability of the allyl group to form either π- or σ-bonded derivatives with certain transition metals.[4]

In contrast to the behavior of palladium which forms numerous π-allyl derivatives, only a few allyl derivatives have been reported for platinum.[5–7]

The reaction of allyl iodide with either the *o*-tolyl or *p*-tolyl derivative of bis(tolyl)bis(pyridine)platinum(II) produced the identical compound, $(C_5H_5N)_2Pt(C_3H_5)_2(I_3)_2$. The ultraviolet spectrum of the product displayed absorption maxima at 295 and 365 mμ indicative of the triiodide ion,[8] and a suspension of the compound in a mixture of 6 *N* hydrochloric acid and carbon tetrachloride slowly liberated elementary iodine.

The compound $[(C_6H_5)_3P]_2Pt(CH_3)I_3$[3] was reinvestigated and the ultraviolet absorption maxima at 295 and 365 mμ were observed. This evidence indicates that this compound is a platinum(II) triiodide complex rather than a platinum(IV) compound as previously reported.

The intense absorption bands associated with the coordinated pyridine in $(C_5H_5N)_2Pt(C_3H_5)_3(I_3)_2$ preclude the assignment of specific absorptions to the allyl group in the carbon–carbon double bond stretching

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[1] To whom inquiries should be addressed at Wisconsin State University.

[2] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 705 (1959).

[3] C. R. Kistner, J. H. Hutchinson, J. R. Doyle, and J. C. Storlie, *Inorg. Chem.*, **2**, 1255 (1963).

[4] For recent reviews of this subject see: (a) M. L. H. Green and P. L. I. Nagy, *Advan. Organometal. Chem.*, **2**, 325 (1964); (b) H. L. Maddox, S. L. Stafford, and H. B. Kaesz, *ibid.*, **3**, 1 (1966); (c) E. O. Fischer and H. Werner, "Metal π-Complexes," Vol. 1, American Elsevier Co., New York, N. Y., 1966.

[5] B. L. Shaw and N. Sheppard, *Chem. Ind.* (London), 517 (1961).

[6] H. C. Vogler and K. Vrieze, *J. Organometal. Chem.* (Amsterdam), **6**, 297 (1966).

[7] G. W. Parshall, *Z. Naturforsch.*, **17b**, 772 (1963).

[8] R. E. Buckles, J. P. Yuk, and A. I. Popov, *J. Am. Chem. Soc.*, **74**, 4379 (1952).

Table I

Properties and Analyses of Products

Product	Formula	Reaction temp, °C	C Calcd	C Found	H Calcd	H Found	N Calcd	N Found	Pt Calcd	Pt Found	Decompn temp, °C	Color and form
			Analyses, %									
Bis(triiodo)bis(allyl)bis(pyridine)-platinum(IV)	$(C_5H_5N)_2Pt(C_3H_5)_2(I_3)_2$	25	16.05	15.96	1.67	1.73	2.34	2.34	16.31	16.76	228 melts and decomposes	Red platelets
Diiodo(ethyl)-*o*-tolylbis(pyridine)-platinum(IV)	$(C_5H_5N)_2PtI_2(C_2H_5)(C_7H_7)$	25	31.38	32.25	3.04	3.30	3.88	3.95	26.82	27.27	131–137	Yellow needles
Iodo(*o*-tolyl)bis(pyridine)-platinum(II)	$(C_5H_5N)_2PtI(C_7H_7)$	25	35.79	36.21	2.99	2.94	4.90	5.03	34.09	33.08	167	Red needles
Diiodo(ethyl)-*p*-tolylbis(pyridine)-platinum(IV)	$(C_5H_5N)_2PtI_2(C_2H_5)(C_7H_7)$	25	31.38	31.88	3.04	3.36	3.88	...	26.82	26.49	147	Yellow needles
Diiodo(*n*-propyl)-*o*-tolylbis(pyridine)platinum(IV)	$(C_5H_5N)_2PtI_2(C_3H_7)(C_7H_7)$	50	32.19	32.61	3.22	3.17	3.78	...	26.26	26.30	134	Yellow needles

region or in the regions previously assigned to the carbon–carbon stretching frequency in π-bonded allyl groups.[9–11]

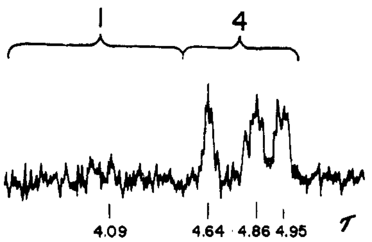

Figure 1.—Allyl resonance from $(C_5H_5N)_2Pt(C_3H_5)_2(I_3)_2$ in deuterated dimethyl sulfoxide at 25°.

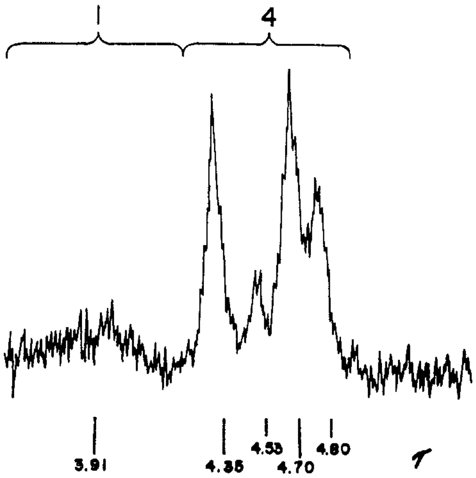

Figure 2.—Allyl resonance from $(C_5H_5N)_2Pt(C_3H_5)_2(I_3)_2$ in tetramethylene sulfone at 25°.

The pmr spectrum in either tetramethylene sulfone or deuterated dimethyl sulfoxide consists of two sets of resonance bands attributable to the coordinated pyridine and the allyl group (relative ratio 1:1). The coordinated pyridine has a complex AB_2C_2 pattern centered at τ 1.61 and similar to the pattern found in *cis*-$(C_5H_5N)_2PtCl_2$ and the recently discussed[12] *trans*-$(C_5H_5N)_2PtCl_2$ except for a shift of all signals to lower τ values. A detailed analysis of this portion of the spectrum was not attempted. The allyl portion of the spectrum appears to be a complex $ABCX_2$ pattern in deuterated dimethyl sulfoxide (Figure 1) and tetramethylene sulfone (Figure 2). A similar pattern has been reported[13] for allyl iodide in which the α protons appear as a well-resolved doublet (τ 6.13), the β proton appears as a complex band of at least 12 lines centered at τ 4.07, and the γ protons appear as a pair of overlapping doublets (τ 4.85 and 4.95). In our compound the β proton appears as a broad, poorly resolved band centered at τ 4.09, and the bands associated with the α and γ protons overlap to yield an asymmetric triplet (τ 4.64, 4.86, and 4.95) when dissolved in deuterated dimethyl sulfoxide (Figure 1). In tetramethylene sulfone (Figure 2) the β-proton band appears as a broad band centered at τ 3.91, and the α and γ protons overlap to yield a complex four-line pattern (τ 4.35, 4.53, 4.70, and 4.80). In both solvents the relative ratio of the β protons to the combined α and γ protons was 1:4. The similarity of the patterns and the τ values in both a strongly coordinating solvent and a weakly coordinating solvent indicate that the so-called "π–σ interconversion" found in palladium–allyl compounds[14] did not occur in this platinum–allyl derivative. The platinum–allyl derivative was recovered unchanged from solutions in deuterated dimethyl sulfoxide or tetramethylene sulfone.

The pattern and chemical shifts associated with the protons of the allyl group favor a σ-bonded configuration and, coupled with the presence of the triiodide ion, indicate a normal six-coordinated platinum(IV) complex.

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(9) W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties, and B. W. Howk, *J. Am. Chem. Soc.*, **83**, 1601 (1961).

(10) M. A. Bennett, G. J. Erskine, J. Lewis, R. Mason, R. S. Nyholm, G. B. Robertson, and A. D. C. Towl, *Chem. Commun.*, 395 (1966).

(11) E. Lanpher, *J. Am. Chem. Soc.*, **79**, 5578 (1957).

(12) R. S. Drago, V. A. Node, and J. G. Kay, *Inorg. Chem.*, **5**, 2050 (1966).

(13) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "N.M.R. Spectra Catalog," Varian Associates, Inc., Palo Alto, Calif., 1962, Spectra No. 24 and 25.

(14) G. L. Stratton and K. C. Ramey, *J. Am. Chem. Soc.*, **88**, 4387 (1966).