## CONC LUSIONS

1. Catalytic phosphorylation of  $\alpha$ -trifluoromethyl-m-trifluoromethylbenzyl alcohol by POCl<sub>3</sub> in the ratio of 2:1 primarily yielded bis( $\alpha$ -trifluoromethyl)m-trifluoromethylbenzyl)chlorophosphate regardless of the conditions of the reaction, and in contrast to unsubstituted  $\alpha$ -trifluoromethylbenzyl alcohol, absolutely no simple benzyl ether was formed.

2. The bis ( $\alpha$ -trifluoromethyl-m-trifluoromethylbenzyl) chlorophosphate obtained is a mixture of three diastereomers in a ratio close to the statistical ratio.

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## REDOX REACTIONS OF MERCURY DERIVATIVES

OF 8-ALKYLQUINOLINES WITH Pd(0) AND Pt(0) COMPLEXES

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Our knowledge of redox demercuration by Pt(0) and Pd(0) complexes, despite the numerous examples studied [1], is incomplete. Specifically, with a single exception [2], no instances are known of the formation in this way of chelatemetallocycles in which the transition metal is bonded with an aliphatic sp<sup>3</sup>-hybridized carbon atom. We encountered the problem of the reactivity of alkylmercury compounds containing a donor nitrogen atom in the  $\gamma$ -position when choosing a model reaction for a study of the stereochemistry of redox demercuration. The chiral 8-( $\alpha$ -bromomercuriethyl)quinoline (I) [3] and its homolog (II) [3] and its homolog (II) have recently been proposed as model compounds



It was expected that the reaction of (I) or (II) with the  $d^{10}$ -complexes  $(Ph_3P)_3Pt$  (III),  $(Ph_3P)_4Pd$  (IV),  $(DBA)_3Pd_2 \cdot CHCl_3$  (V)\* or  $(DBA)_2Pd$  (VI) would afford, following replacement of the mercury, the chelate metal-

\* DBA is dibenzylideneacetone.

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Fig. 1. General view of the triphenylphosphine (8-methylquinoline-C,N)palladium bromide molecule (from x-ray data).

TABLE 1. Principal Interatomic Distances and Angles in Triphenylphosphine-(8-methylquinoline-C,N)palladium Bromide

Bond	Length, Å	Angle	ω <b>, de</b> g
Pd-Br	2,590 (09)	NPdBr	91,84(1,10)
Pd-P	2,256 (16)	NPdC	88,82(1,81)
Pd-N	2,126 (43)	BrPdP	91,77(0,44)
Pd-C	2,139 (49)	PPdC	87,5(1,51)

locycles. Metallocycles derived from 8-alkylquinolines, including optically active compounds, are known. They were obtained by the direct metallation of the alkyl group [4, 5], or by the oxidative addition of bromides to the Pt(0) complex [6-8]. These compounds are much more stable than open-chain acyclic alkyl Pd and Pt complexes. The reason for this is that chelation makes impossible the adoption of conformations favoring the elimination of the  $\beta$ -hydrogen atom.

We have found that (I) and (II) react rapidly with (IV) in benzene with the complete elimination of mercury



The complexes triphenylphosphine-(8-ethylquinoline- $\alpha$ -C,N)palladium bromide (VII) and triphenylphosphine-(8-methylquinoline-C,N)palladium bromide (VIII) are yellow in color, stable in air, soluble in benzene, chloroform, and acetone, and crystallize well. PMR and IR spectra were obtained for these and the other chelate complexes described. The <sup>31</sup>P-{<sup>1</sup>H} NMR spectrum of (VII) contains a solitary singlet, indicating the formation of a single isomer. The trans-arrangement of the phosphine ligand with respect to nitrogen in the coordination sphere of palladium follows from x-ray structural analysis (Fig. 1). The structural parameters for the complex (VIII) are given in Table 1.

Similarly, reaction of (I) or (II) with dibenzylideneacetone complexes of Pd(0) affords the metal halide dimers (IX) and (X).



R = Me (IX); H (X), (XI).

The reaction of (I) with (V) was carried out in benzene, and that of (II) with (VI) in THF, since in benzene the yield of (X) was no greater than 8%.

The high degree of conversion of (I) into chelate metallocycles on treatment with Pd(0) triphenylphosphine and dibenzylideneacetone complexes enabled us to choose these reactions as models for the study of the stereochemistry of redox demercuration [9].

The reaction of (I) and (II) with (III) is unusual, since in addition to triphenylphosphine-(8-methylquinoline C,N)platinum bromide (XII) (54%), (II) also afforded the platinum dibromide (XIII).



With (III), the mercury compound (I) gives exclusively (XIII) (yield 91%).

In none of the reactions considered here was there any evidence of the formation of a dimetallic intermediate, and alternative mechanisms involving  $S_N^2$  substitution, in which M(0) functions as the nucleophile, are therefore proposed.\* Such a route has been considered previously, [10, 11] for the oxidative addition of benzyl halides to palladium phosphine complexes, and for 8-( $\alpha$ -bromoethyl)quinoline [8] with (III). In these optically active models, inversion of configuration occurred at the reaction center, viz., the benzyl carbon. Another possible route may be represented as follows:

$$RHgBr + L_nM(0) \rightarrow L_mMBr + Hg(0) + R^{\bullet}$$

Subsequently, one of the following reactions takes place:

A. The radical pair ( $L_m M^{\circ}Br$ ), (R<sup>•</sup>) may collapse with the formation of the normal adduct, namely, a compound with an M-C  $\sigma$  bond (a chelate metallocycle).

B. The intermediate  $(L_m M^{\circ}Br)$  detaches halogen from a second molecule of the mercury compound, and is converted into the dibromide (XIII), and dimerization of (R') gives R-R.

In the case of 8-( $\alpha$ -bromomercuriethyl)quinoline and (Ph<sub>3</sub>P)<sub>3</sub>Pt, pathway B predominates. The formation of a mixture of erythro- and threo-2,3-di-(8-quinolinyl)butanes (XIV) and dimerization products of the benzyl radical were confirmed by the NMR spectrum <sup>13</sup>C-{<sup>1</sup>H}:  $\delta$  CH<sub>3</sub> 22.16, 21.19;  $\delta$ CH 37.64, 36.72, together with the mass spectrum: M<sup>+</sup> 312.

#### EXPERIMENTAL

Reactions with tetrakis(triphenylphosphine)palladium (IV), tris(triphenylphosphine)palladium (III), and the Pd(0) dibenzylideneacetone complexes (V) and (VI) were carried out under argon. Solvents were purified and degassed. PMR spectra were obtained on a Bruker WP-200-SY, operating frequency 200.13 MHz, internal standard TMS. IR spectra were obtained on a UR-10 instrument.

8-(α-Bromomercuriethyl)quinoline (I) was obtained as described in [9]. Yield 68%, mp 152°C (decomp.). PMR spectrum (CDCl<sub>3</sub>, δ, ppm): 1.86 d (CH<sub>3</sub>),  ${}^{3}J_{HH} = 7.4$ ,  ${}^{3}J_{HHg} = 274.8$  Hz, 3.89 q (CH),  ${}^{2}J_{HHg} = 269.9$ , 7.44– 8.20 m (H<sup>3</sup>-H<sup>7</sup>), 8.91 q (H<sup>2</sup>). IR spectrum (KBr, ν, cm<sup>-1</sup>): 3062 med. (quinoline), 2975, 2948, 2916, 2868 (CH and CH<sub>3</sub>).

<u>8-(Bromomercurimethylquinoline (II)</u> was obtained similarly [3]. Yield 28%, mp 157°C (from heptane). PMR spectrum (pyridine- $d_5$ ,  $\delta$ , ppm): 3.49 s (CH<sub>2</sub>),  ${}^2J_{HHg} = 270.6$  Hz. IR spectrum (KBr,  $\nu$ , cm<sup>-1</sup>): 425, 490, 580, 610, 655, 686, 708, 755, 800, 830, 890, 1055, 1100, 1142, 1175, 1315, 1380, 1395, 1430, 1475, 1505, 2938, 2975, 3060.

 ${}^{ar{*}}$  Stereochemical proof of the  ${
m S_N2}$  mechanism for the reaction of (I) with (IV) will be published elsewhere.

<u>Triphenylphosphine-(8-ethylquinoline- $\alpha$ -C,N)palladium Bromide (VII).</u> To a solution of 1.15 g (1.0 mmole) of (IV) in 30 ml of benzene was added 0.42 g (0.96 mmole) of (I) with stirring. After 10 min, mercury separated, and the color of the solution changed from orange to pale yellow. After 1 h, the solution was filtered from the solid, and 30 ml of hexane was added. The pale yellow solid which separated on cooling was isolated, washed with hexane, and dried in vacuo to give 0.46 g (79%) of (VII), decomp. 125-130°C (from benzene). Found: C 61.29; H 4.73; Br 12.36; P 4.91%. C<sub>29</sub>H<sub>25</sub>BrNPPd  $\cdot$ C<sub>6</sub>H<sub>6</sub>. Calculated: C 61.55; H 4.34; Br 11.70; P 4.53%. PMR spectrum (CDCl<sub>3</sub>,  $\delta$ , ppm): 1.01 t (CH<sub>3</sub>), <sup>4</sup>J<sub>HP</sub>=<sup>3</sup>J<sub>HH</sub>=7.1 Hz, 3.12 m (CH), 7.37-8.27 m (H<sup>3</sup>-H<sup>7</sup> of the quinoline ring and the PPh<sub>3</sub> protons), and 9.96 m (H<sup>2</sup> of quinoline). <sup>31</sup>P-{<sup>1</sup>H} NMR spectrum (CH<sub>2</sub>Cl<sub>2</sub>,  $\delta$ , ppm): 34.8. IR spectrum (KBr,  $\nu$ , cm<sup>-1</sup>): 3070, 3040, 2970, 2900, 2875, 2850 (cf. [1]).

<u>Triphenylphosphine-(8-methylquinoline-C,N)palladium Bromide (VIII)</u>. To a solution of 1.2 g (1.04 mole) of (IV) in 30 ml of benzene was added 0.42 g (1 mmole) of (II). The Pd complex was isolated as for (VII), to give 0.54 g (86%) of (VIII), mp 207°C (from benzene). Found: C 58.98; H 4.26; Br 12.29%. C<sub>28</sub>H<sub>23</sub>BrNPPd· $^{1}/_{2}C_{6}H_{6}$ . Calculated: C 59.10; H 4.16; Br 12.69%. PMR spectrum (CDCl<sub>3</sub>,  $\delta$ , ppm): 3.04 d (CH<sub>2</sub>),  $^{3}J_{HP}=4.0$  Hz, IR spectrum (KBr,  $\nu$ , cm<sup>-1</sup>): 3054, m, 2935, 2884. Preliminary x-ray structural studies were carried out on (VIII). Monocrystals were purified from a mixture of benzene and hexane. The cell parameters and intensities of 4552 reflections were measured on a Syntex P2<sub>1</sub> automatic 4-circle diffractometer ( $\lambda$  MoK<sub> $\alpha$ </sub>). The crystals were triclinic, *a*=17.983(1), b=12.460(8), c=12.919(2) A°,  $\alpha$ =90.24(7)°,  $\beta$ =109.92(8)°,  $\gamma$ =98.60(8)°; V=2686.2 Å<sup>3</sup>; space group P1, d<sub>calc</sub>=1.49 g/cm<sup>3</sup>, Z=4.

The structure was interpreted by the heavy-atom method. In the interpretation and refinement of the structure, 2236 independent reflexions with  $I \ge 15 \sigma$ , R = 0.1334 are used. All the calculations were carried out on a BÉSM-6 computer with the Rentgen-75 program [12].

<u>Di- $\mu$ -bromobis-(8-ethylquinoline- $\alpha$ -C,N)dipalladium (IX).</u> In 50 ml of benzene there were dissolved 1.3 g (1.3 mmole) of (V) and 1.0 g (2.3 mmole) of (I). Over a period of 1.5 h, the deep violet color of the solution changed to pale yellow. The solution was filtered from the solid (0.05 g), and on cooling the filtrate yellow crystals (0.56 g) of (IX) separated. The mother liquor was evaporated to dryness, and the residue washed with ether to remove DBA to give 0.05 g of the complex. Total yield of (IX) 0.61 g (81%), mp 164°C (decomp.), darkens at 147°C. Found: C 38.69; H 3.20%. C<sub>22</sub>H<sub>20</sub>Br<sub>2</sub>N<sub>2</sub>Pd<sub>2</sub>. Calculated: PMR spectrum, (CDCl<sub>3</sub>,  $\delta$ , ppm): 1.36 d (CH<sub>3</sub>), <sup>3</sup>J<sub>HH</sub> = 7.4 Hz; 4.59 q (CH), 7.35-8.29 m (quinoline H<sup>3</sup>-H<sup>7</sup>); 9.13 d.d. (quinoline H<sup>2</sup>). IR spectrum (KBr,  $\nu$ , cm<sup>-1</sup>): 3075, 2970, 2945, 2900, 2845.

<u>Di- $\mu$ -bromobis-(8-methylquinoline-C,N)dipalladium (X).</u> In 12 ml of THF there were dissolved 0.42 g (1 mmole) of (II) and 0.60 g (1.04 mmole) of (VI). The reddish-violet color of the solution changed over a period of five minutes to orange. The solution was filtered from a black solid, and the solid washed with 30 ml of chloroform and dried to give 0.28 g of solid (Hg and Pd). The solution was combined with the chloroform extract, evaporated to 1/3 of its volume, and diluted with 50 ml of ether, whereupon a red solid separated. This was washed with benzene and dried in vacuo to give 0.18 g (55%) of (X), decomp. 216-217°C. For elemental analysis, (X) was converted into its pyridine complex (XI) which was crystallized from ether, mp 230°C. Found: C 44.18; H 3.46; Br 18.86%. C<sub>15</sub>H<sub>13</sub>BrN<sub>2</sub>Pd. Calculated: C 44.20; H 3.22; Br 19.60%. PMR spectrum (pyridine-d<sub>5</sub>,  $\delta$ , ppm): 3.56 s (CH<sub>2</sub>). IR spectrum (KBr,  $\nu$ , cm<sup>-1</sup>): 3065, 3014, 2930, 2892.

<u>Triphenylphosphine-(8-methylquinoline-C,N)platinum Bromide (XII).</u> To a suspension of 0.23 g (0.54 mmole) of (II) in 20 ml of benzene was added 0.55 g (0.56 mmole) of (III), and the mixture was stirred. The orange color of the solution disappeared, and mercury separated. After 24 h, the solution was filtered from the solid (0.12 g) and evaporated in vacuo. The complex (XII) was separated from the dibromide (XIII) (0.125 g, 25%) by treating the solid with 20 ml of benzene. The benzene solution was diluted with pentane, and the light yellow crystalline solid which separated was filtered off and dried in vacuo to give 0.21 g (54%) of (XII). The compound crystallized as a solvate with benzene, decomp. 128°C, mp 227°C. Found: C 52.53; H 3.57; Br 10.87%. C<sub>28</sub>H<sub>23</sub>BrNPPt  $^{1/2}C_{6}H_{6}$ . Calculated: C 51.80; H 3.64; Br 11.12%. Solvate with chloroform, mp 229°C. Found: C 46.74; H 3.13; N 2.01; Cl+Br 17.88%. C<sub>28</sub>H<sub>23</sub>BNPPt  $^{1/2}CHCl_3$ . Calculated: C 46.31; H 3.20; N 1.89; Cl+Br 18.01%. PMR spectrum (CDCl<sub>3</sub>,  $\delta$ , ppm): 2.78 d (CH<sub>3</sub>),  $^{3}J_{HP}=3$ ,  $^{2}J_{HPt}=65.9$  Hz, 7.24-8.30 m (quinoline H<sup>3</sup>-H<sup>7</sup>), 10.32 m (quinoline H<sup>2</sup>),  $^{2}J_{HPt}=31.9$  Hz. IR spectrum (KBr,  $\nu$ , cm<sup>-1</sup>): 3065, 2922, 2870.

Reaction of 8-( $\alpha$ -Bromomercuriethyl)quinoline with (III). In 25 ml of benzene there were dissolved 0.85 g (2 mmole) of (I) and 1.93 g (2 mmole) of (III). After 65 h, the solid was separated from the solution. Extraction of the solid, which contained mercury, with CH<sub>2</sub>Cl<sub>2</sub> afforded 0.78 g (91% in solution on (I)) of (III), mp 307°C (decomp.). Weight of mercury, 0.394 g. Found: C 48.31; H 3.45%. C<sub>36</sub>H<sub>30</sub>Br<sub>2</sub>P<sub>2</sub>Pt. Calculated: C 49.16; H 3.44%. IR spectrum (KBr,  $\nu$ , cm<sup>-1</sup>): 417, 458, 503, 518, 530, 550, 623, 700, 745, 755, 858, 930, 1003, 1032, 1078, 1100, 1165, 1190, 1285, 1315, 1438, 1482, 1572, 1588, 3058. The filtrate was evaporated to the smallest possible

volume, and hexane was added, whereupon a mixture of compounds separated. According to TLC (Silufol, eluant benzene-triethylamine, 3:1), the mixture contained at least four compounds,  $R_f$  0.91, 0.78, 0.64, and 0.10. The mixture was partially separated on silica gel L100/160 plates. Triphenylphosphine ( $R_f$  0.91) was eluted with benzene. Elution with a 3:1 mixture of benzene and triethylamine afforded (XIV) ( $R_f$  0.64). Mass spectrum (70 eV, 40°C, m/z): 312 M<sup>+</sup>; 156 (base peak). <sup>13</sup>C-{<sup>1</sup>H} NMR spectrum (CCl<sub>4</sub>,  $\delta$ , ppm): 21.19 and 22.16, two singlets (CH<sub>3</sub>), 36.72 and 37.64 two singlets (CH), 120-148 m (quinoline carbons).

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## CONCLUSIONS

1. Redox demercuration of mercury derivatives of 8-alkylquinolines by Pd(0) and Pt(0) complexes affords 5-membered chelate metallocycles, except for the reaction between  $8-(\alpha-bromomercuriethyl)$ quinoline and  $(Ph_3P)_3Pt$ .

2. X-ray structural analysis of the triphenylphosphine-(8-methylquinoline-C,N)palladium bromide molecule has shown that the phosphine ligand is trans-oriented to the nitrogen atom in the Pd coordination sphere.

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