REACTIONS OF CYCLOALKYLMERCURIC BROMIDES WITH A TRIPHENYLPHOSPHINE COMPLEX OF ZEROVALENT PLATINUM

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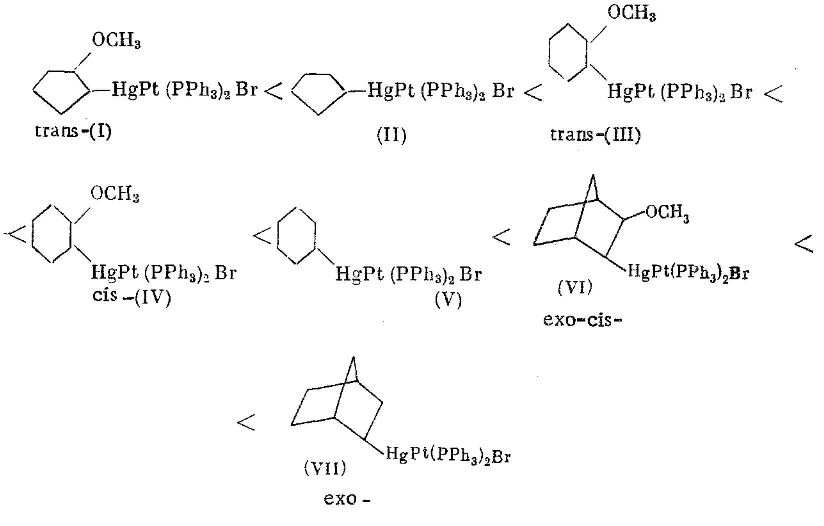
In a study of the applicability and mechanism of reactions of organomercury compounds with complexes of zerovalent platinum group metals [1], we found that cycloalkylmercuric halides in which mercury is bonded to a secondary carbon react with $Pt(PPh_3)_3$ to form, depending on the reaction conditions, compounds with an Hg−Pt bond* or cycloalkyl derivatives of platinum

$$RHgBr + Pt(PPh_3)_3 \xrightarrow[-PPh_3]{} RHgPt(PPh_3)_2Br \xrightarrow[-Hg]{\text{Sunlight}} RPt(PPh_3)_2Br$$

where R is cyclopentyl, 2-methoxycyclopentyl, cyclohexyl, trans-2-methoxycyclohexyl, cis-2-methoxycyclohexyl, exo-norbornyl, or exo-cis-methoxynorbornyl.

We suggested that compounds with an Hg−Pt bond may be intermediates in the reaction of organomercury compounds with $Pt(O)L_n$ [1] and rigorously demonstrated this in several cases [2]. Platinum−mercury compounds are most stable when electron-accepting groups (CF_3, C_6F_5, etc.) are present in the molecule [3, 4].

We have prepared compounds with an Hg−Pt bond by reaction in the dark of cycloalkylmercuric bromides; these are readily photolyzed, eliminating mercury. Reaction of CF_3COOH with these and other compounds with an Hg−Pt bond [5] results in elimination of mercury. In the photolysis of platinum−mercury compounds in benzene solution, the cyclopentyl derivatives most readily eliminate mercury; their stability increases in the order



trans-(I) (II) trans-(III) cis-(IV) (V) (VI) exo-cis- (VII) exo-

The elimination of Hg is complete within 5 h to 5 days, depending on the structure of the cycloalky moiety. After deposition of Hg in the photolysis of cycloalkylmercuric bromides with $Pt(PPh_3)_3$ we were able to isolate the relatively stable σ-cycloalkylplatinum complexes from the benzene solution.

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*We consider that the more probable order of bonding is R−Hg−Pt−Br, although we cannot exclude the alternative, Br−Hg−PtR.

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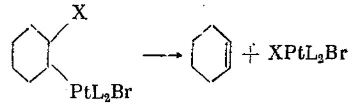
TABLE 1. [(σ-Cycloalkyl)mercuri] platinum Compounds Prepared by Reaction of Cycloalkylmercuric Bromides with $Pt(PPh_3)_3$

Compound	Yield, %	Decomposition point, °C	Found, %				Emperical formula	Calculated, %			
			C	H	Br	Hg		C	H	Br	Hg
(I)	76	114	45,67	4,03			$C_{42}H_{41}BrHgOP_2Pt$	45,75	3,82		
(II) *	62	136	47,34	3,83	7,30	16,87	$C_{41}H_{39}HgBrP_2Pt \cdot 0{,}5CH_3C_6H_5$	47,91	3,88	7,16	17,98
(III)	85	129	47,89	3,98	6,80	16,76	$C_{43}H_{43}BrHgOP_2Pt \cdot 0{,}5CH_3C_6H_5$	47,89	4,03	6,89	17,13
(IV)	94	145	47,97	3,77	6,90	16,08	$C_{43}H_{43}BrHgOP_2Pt \cdot 0{,}5CH_3C_6H_5$	47,89	4,03	6,89	17,13
(V)	93	152	48,14	4,03	7,09	16,38	$C_{42}H_{41}BrHgP_2Pt \cdot 0{,}5CH_3C_6H_5$	48,34	4,10	7,07	17,74
(VI)	91	148	47,61	3,97	7,17	17,02	$C_{44}H_{43}BrHgOP_2Pt \cdot 0{,}5CH_3C_6H_5$	48,70	4,04	6,82	17,12
(VII)	88	216	47,58	3,97	7,12	17,17	$C_{43}H_{41}BrHgP_2Pt \cdot 0{,}5CH_3C_6H_5$	48,92	3,97	7,00	17,57

*PMR spectrum confirmed the presence of toluene of crystallization.

Thus we isolated σ-cycloalkylplatinum compounds from the photolysis of compounds (III) and (IV) in benzene at 6°C in yields of 64% and 32%, respectively. Earlier attempts to prepare compounds in which platinum is bonded to a secondary carbon atom using organomagnesium compounds [6] or by oxidative addition [7] obtained elimination products: the hydride $HPt(PPh_3)_2Hal$ and the corresponding olefins. This was attributed to the susceptibility of alkyl compounds of platinum to β-elimination. We naturally expected that our synthetic cycloalkylplatinum compounds would behave similarly. Indeed after chromatography or thermolysis of (2-methoxycyclohexyl)bis(triphenylphosphine)platinum bromides (IX) and (X), cyclohexylbis(triphenylphosphine)-platinum bromide (VIII), and cyclopentylbis(triphenylphosphine)platinum bromide (XI), we were able to confirm the formation of hydridobis(triphenylphosphine)platinum bromide [IR spectrum: δ 820, ν 2220 cm^{-1}] [8] and to isolate this compound. We prepared methoxybis(triphenylphosphine)platinum bromide from compound (IX), which has a β-CH_3O group



$X = H, CH_3O, L = PPh_3$

We confirmed that cyclohexane is formed in the decomposition of compounds (VIII), (IX), and (X) by GLC.

Thus we have demonstrated that cycloalkylmercuric bromides in which mercury is bonded to a secondary carbon atom react with $Pt(PPh_3)_3$ and have confirmed that formation of the σ-organoplatinum products involves the intermediacy of platinum–mercury compounds. This expands our view of the applicability of the reaction of organomercury compounds with complexes of zerovalent platinum group metals.

EXPERIMENTAL

All reactions and isolation of products were carried out in an atmosphere of Ar. Spectra were recorded with a Hitachi–Perkin–Elmer R-20 instrument at 60 MHz (PMR); a UR-10 instrument (IR). Melting points were determined in sealed capillaries.

Synthesis of (Cyclohexylmercuri)bis(triphenylphosphine)platinum Bromide (V). To a suspension of $C_6H_{11}HgBr$ (0.18 g, 0.5 mmole) in toluene (25 ml) at 10°C was added $Pt(PPh_3)_3$ (0.50 g, 0.5 mmole); the mixture was stirred until the components had completely dissolved, avoiding exposure to direct sunlight, and then kept in a refrigerator at 0°C for a day. The toluene solution was separated from the small precipitate by filtration. Addition of cold hexane (60 ml) gave a light-yellow precipitate, which was separated and washed with benzene–hexane (1:20) (3 × 5 ml). After drying under vacuum the weight of the product was 0.51 g (93%). The compound decomposed at > 152°C (in a sealed capillary). The other platinum–mercury derivatives of cycloalkanes (Table 1) were prepared in the same way.

IR Spectra* (KBr, cm^{-1}).

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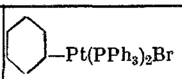
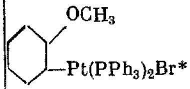
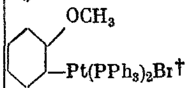
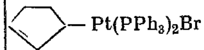
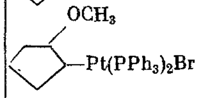
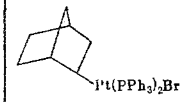
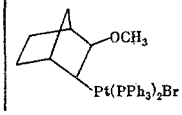
*s = strong; m = medium; w = weak.

TABLE 2. (σ-Cycloalkyl)platinum Compounds Prepared by Reaction of Cycloalkylmercuric Bromides with $Pt(PPh_3)_3$

Compound	Formula	Yield, %	Decomp. point °C	Empirical formula	Found, %	Calculated, %
(VIII)		86,3	136	$C_{42}H_{41}PtP_2Br$	C 56,24 H 4,32 Br 9,01	C 57,11 H 4,67 Br 9,07
(IX)		73,3	112	$C_{43}H_{43}PtOP_2Br$	C 57,83 H 4,10 Br 9,76	C 56,58 H 4,74 Br 8,64
(X)		69	112	$C_{43}H_{43}PtOP_2Br$	C 57,98 H 4,11 Br 9,44	C 56,58 H 4,74 Br 8,64
(XI)		72	102	$C_{41}H_{39}PtP_2Br$	C 56,64 H 4,35 Br 7,14	C 56,67 H 4,49 Br 8,98
(XII)		52	96	$C_{42}H_{41}PtOP_2Br$	C 57,01 H 4,14 Br 9,49	C 56,12 H 4,56 Br 8,90
(XIII)		76,7	197	$C_{43}H_{41}PtP_2Br$	C 57,64 H 4,62 Br 9,48	C 56,56 H 4,79 Br 8,93
(XIV)		76,4	160	$C_{44}H_{43}PtOP_2Br$	C 56,21 H 4,55 Br 9,19	C 57,15 H 4,76 Br 8,65

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*Prepared from (trans-2-methoxycyclohexyl)mercuric bromide and $Pt(PPh_3)_3$.

†Prepared from (cis-2-methoxycyclohexyl)mercuric bromide and $Pt(PPh_3)_3$.

[(trans-2-Methoxycyclopentyl)mercuri]bis(triphenylphosphine)platinum bromide (I): 505 s, 525 s, 545 s, 690 c, 1085 s, 1434 s, 2820 s, 620 m, 585 m, 1155 m, 1480 m, 2845 m, 3050 m, 3070 m, 640 w, 765 w, 842 w, 918 w, 995 w, 1024 w, 1082 w, 1092 w, 1115 w, 1305 w.

[(trans-2-Methoxycyclohexyl)mercuri]bis(triphenylphosphine)platinum bromide (III): 530 s, 546 s, 690 s, 700 s, 770 s, 2830 s, 422 m, 1075 m, 1000 m, 1032 m, 1155 m, 1188 m, 2824 m, 2855 m, 3069 m, 590 w, 615 w, 645 w, 855 w, 890 w, 925 w, 1250 w, 1280 w, 1312 w.

[(cis-2-Methoxycyclohexyl)mercuri]bis(triphenylphosphine)platinum bromide (IV): 525 s, 535 s, 690 s, 740 s, 1090 s, 2815 s, 2825 s, 415 m, 588 m, 675 m, 995 m, 1025 m, 1180 m, 3055 m, 3062 m, 2850 m, 3070 m, 640 w, 665 w, 780 w, 835 w, 825 w, 930 w, 1115 w, 1130 w, 1285 w, 1355 w.

(Cyclohexylmercuri)bis(triphenylphosphine)platinum bromide (V): 500 s, 524 s, 692 s, 745 s, 1432 s, 2819 s, 622 m, 588 m, 1158 m, 1480 m, 2845 m, 3050 m, 3070 m, 640 w, 765 w, 840 w, 925 w, 980 w, 998 w, 1025 w, 1085 w, 1115 w, 1309 w.

[(exo-cis-Methoxynorbornyl)mercuri]bis(triphenylphosphine)platinum bromide (VI): 498 s, 524 s, 538 s, 690 s, 1090 s, 1430 s, 738 m, 1065 m, 1475 m, 2864 m, 2915 m, 2948 m, 3068 m, 415 w, 585 w, 635 w, 860 w, 915 w, 935 w, 970 w, 995 w, 1025 w, 1145 w, 1120 w, 1145 w, 1218 w, 1240 w, 1310 w, 2812 w, 3000 w.

[(exo-Norbornyl)mercuri]bis(triphenylphosphine)platinum bromide (VII): 500 s, 522 s, 535 s, 692 s, 785 s, 750 s, 736 m, 1065 m, 1474 m, 2948 m, 3050 m, 418 w, 528 w, 632 w, 682 w, 915 w, 936 w, 972 w, 994 w, 1025 w, 1120 w, 1145 w, 1245 w, 1220 w, 1294 w, 1312 w, 3000 w.

Synthesis of Cyclohexylbis(triphenylphosphine)platinum Bromide (VIII). The elimination of Hg (95 mg, 95%) in the photolysis of a solution of $C_6H_{11}HgBr$ (0.18 g, 0.5 mmole) and $Pt(PPh_3)_3$ (0.50 g, 0.5 mmole) in benzene (30 ml) was complete after 6 h. The solution contained only one platinum compound [TLC; (Rf 0.57); Silufol; benzene–ethyl acetate (3:1)]. The solution was separated from Hg by filtration, and cold hexane (80 ml) was added to the filtrate. The light-yellow crystalline precipitate was washed with benzene–hexane (1:15) and dried under vacuum to give (VIII) (0.38 g, 86%), decomposition point 136°C. The other cycloalkylplatinum derivatives (Table 2) were prepared in the same way.

Photolysis of Cyclohexylbis(triphenylphosphine)platinum Bromide (VIII). Chromatography on a column packed with silica gel L 100/160 μ (20 g) [toluene–ethyl acetate (3:1)] of the reaction product from photolysis of cyclohexylmercuric bromide (0.36 g, 1 mmole) with $Pt(PPh_3)_3$ (0.98 g, 1 mmole) gave hydridobis(triphenylphosphine)platinum bromide (0.31 g, 37%), mp 178°C (from toluene–hexane). The substance contained toluene of crystallization. PMR spectrum (δ, ppm); 2.07 (CH_3). IR spectrum (KBr): δ 820, ν 2220 cm^{-1} (Pt–H). Found: C 58.03; H 4.13; Br 9.48%. $C_{36}H_{31}BrP_2Pt \cdot CH_3C_6H_5$. Calculated: C 57.92; H 4.40; Br 8.95%.

Photolysis of (2-Methoxycyclohexyl)bis(triphenylphosphine)platinum Bromide (IX). Photolysis of (IX), carried out under the conditions of the preceding reaction, gave methoxybis(triphenylphosphine)platinum bromide in 47% yield, mp 210°C (decomposition). PMR spectrum ($CHCl_3$, δ, ppm); 2.32 unresolved multiplet (OCH_3). Found: C 53.93; H 4.05; Br 10.35%. $C_{37}H_{33}BrOP_2Pt$. Calculated: C 53.49; H 3.98; Br 9.64%.

CONCLUSIONS

1. The reaction of cycloalkylmercuric bromides with $Pt(PPh_3)_3$ involves the intermediacy of compounds with an Hg–Pt bond, which can be isolated in the dark at low temperatures (0-10°C).

2. Photolysis of the platinum mercury compounds in solution forms (σ-cycloalkyl)bis(triphenylphosphine)platinum bromides. These are the first reported σ-platinum derivatives with the metal bonded to a secondary carbon atom.

3. (σ-Cycloalkyl)bis(triphenylphosphine)platinum bromides decompose by β-elimination.

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