Journal of Organometallic Chemistry, 164 (1979) 259—275

ALLYLMERCURY COMPOUNDS, CONVENIENT REAGENTS FOR SYNTHESIS OF π-ALLYL DERIVATIVES OF TRANSITION METALS

A.N. NESMEYANOV and A.Z. RUBEZHOV *

Institute of Organo-Element Compounds, U.S.S.R. Academy of Sciences, Moscow, 117813, Vavilova 28 (U.S.S.R.)

(Received June 28th, 1978)

Summary

The reactions of allylmercury halides RC_3H_4HgX with salts and complexes of platinum metals were studied. Allylmercury compounds were found to be universal allylating reagents and were used to synthesize π-allyl complexes of rhodium, iridium, osmium, ruthenium and platinum. The mechanism of allylation is discussed for the interaction of allylmercury halide with palladium acetate.

Introduction

A variety of methods are used to synthesize π-allyl complexes of platinum metals (see survey in ref. 1). However, there is no standard method which could be used to obtain under comparable conditions π-allyl derivatives of a whole series of metals from available compounds. Attempts were made to use allyl compounds of Sn [2], Tl [3], Si [4] as such universal allylating reagents, but, at best, only allylation of one or two of the six platinum metals was successful. The disadvantage of allyl derivatives of Sn, Tl and Si is that they are obtained from the corresponding Grignard reagents which, in their turn, are synthesized from allyl halides. Thus, the availability of substituted allyl halides restricts the number of π-allyl complexes that may be prepared from allyl compounds of Sn, Tl and Si. At present allylmercury compounds with various substituents in the allyl group have become accessible [5]. The present paper summarizes results which we have obtained in the study of reactions of allylmercury halides with salts and complexes of platinum metals (see ref. 6—14).

Experimental

Allylmercury compounds were obtained from the corresponding allylpalladium halides and metallic mercury [5]; initial complexes of platinum metals were prepared according to well-known techniques. IR spectra were recorded on a UR-10 instrument in KBr pellets. PMR spectra were studied on R-12 and RYa-2305 spectrometers in solutions of benzene, deuterochloroform and deuteroacetone.

Reaction of allylmercury chloride with Na_2PdCl_4

A colorless solution of 2 g (0.0082 mol) of allylmercury chloride in 100 ml of CH_3OH was added to a transparent red solution of 2.12 g (0.0072 mol) of Na_2PdCl_4 in 100 ml of a CH_3OH/H_2O mixture (1/1) and mixed at room temperature for 5 min. The mixture was filtered, the filtrate washed with water and extracted with CH_2Cl_2. The extract was then washed with water, dried over $MgSO_4$ and evaporated. Recrystallization of the residue from benzene/heptane mixture (3/1) yielded 1.02 g of bis(π-allylpalladium chloride) (78%); decomp. 166—169°C. IR spectrum: 3080, 1460, 1380, 1235, 1200, 1000, 970, 950, 770, 970, 950, 770, 515 cm^{-1}.

Reaction of allylmercury chloride with $(NH_4)_2PdCl_4$

Under similar conditions as the previous experiment 0.87 g (95%) of the adduct $C_3H_5PdCl \cdot HgCl_2$ was obtained, decomp. 128—131°C. Found: C, 8.23; H, 1.20; Cl, 23.87; Hg, 43.58; Pd, 22.88. $C_3H_5HgCl_3Pd$ calcd.: C, 7.93; H, 1.11; Cl, 23.40; Hg, 44.14; Pd, 23.41%. IR spectrum: 3590, 3530, 1620, 1460, 1380, 1235, 1220, 1030, 1000, 970, 950, 920, 770, 465 cm^{-1}.

Reaction of allylmercury bromide with K_2PdBr_4

Under similar conditions as the previous experiment 0.78 g (95%) of the adduct $C_3H_5PdBr \cdot HgBr_2$ was obtained, m.p. 144—147°C (decomp.). Found: C, 5.85; H, 0.97; Br, 40.94; Pd, 17.61. $C_3H_5Br_3HgPd$ calcd.: C, 6.13; H, 0.85; Br, 40.89; Pd, 18.06%. IR spectrum: 3590, 3530, 3080, 1620, 1460, 1380, 1235, 1200, 1030, 1000, 970, 950, 920, 770, 465 cm^{-1}.

Reaction of allylmercury bromide with Na_2PdCl_4

Under similar conditions as the previous experiment 1.14 g (68%) of the adduct $C_3H_5PdCl \cdot HgBr_2$ was obtained, m.p. 125—129°C (decomp.). Found: C, 6.88; H, 1.00. $C_3H_5Br_2ClHgPd$ calcd.: C, 6.61; H, 0.93%. IR spectrum: 3590, 3530, 3080, 1620, 1460, 1380, 1235, 1200, 1030, 1000, 970, 950, 920, 770, 465 cm^{-1}.

Reaction of allylmercury chloride with $Pd(OCOCH_3)_2$

Under similar conditions as the previous experiment 0.63 g (70%) of bis(π-allylpalladium acetate) was obtained, m.p. 181—183°C (decomp.). Found: C, 25.49; H, 3.41. $C_{10}H_{16}O_4Pd$ calcd.: C, 25.18; H, 3.38%. IR spectrum: 3070, 3010, 2940, 1680, 1570, 1480, 1390, 1240, 1200, 1080, 1030, 1000, 980, 970, 920, 780, 700, 630, 510 cm^{-1}.

Reaction of allylmercury halides with Na_3RhCl_6 (general technique)

0.0025 *M* of Na_3RhCl_6 in a CH_3OH/H_2O mixture (5/1) was added to a solution of 0.005 *M* of allylmercury halide in 25 ml of CH_3OH. The cherry-red mixture was stirred for 5 h at 25°C and then stored for 10 h at this temperature. The yellow solution was filtered to remove NaCl, the filtrate was diluted with water and extracted with CH_2Cl_2. After drying the organic phase over $MgSO_4$ and removal of the solvent, allylrhodium compounds were obtained which were recrystallized from benzene/heptane. Using this method we prepared: Bis(π-allylrhodium chloride), $[(\pi\text{-}C_3H_5)_2RhCl]_2$. 0.5 g (89%), m.p. 181—183°C (decomp.). Found: C, 32.60; H, 4.57; Cl, 16.05; Rh, 46.78. $C_{12}H_{20}Rh_2Cl_2$ calcd.: C, 32.68; H, 4.57; Cl, 16.10; Rh, 46.67%. IR spectrum: 3105, 3065, 3035, 3005, 1470, 1400, 1255, 1200, 1025, 1005, 475, 920, 910, 820, 745, 570, 550 cm^{-1}.

Bis(π-methallylrhodium chloride), $[(\pi\text{-}2\text{-}MeC_3H_4)_2RhCl]_2$. 0.55 g (78%), m.p. 162—164°C (decomp.). Found: C, 38.92; H, 5.67. $C_{16}H_{28}Rh_2Cl_2$ calcd.: C, 38.66; H, 5.68%. IR spectrum: 3090, 3065, 3030, 2980, 2955, 2920, 1450, 1430, 1385, 1330, 1035, 980, 910, 840, 765, 570 cm^{-1}.

Bis(π-crotylrhodium chloride), $[(\pi\text{-}1\text{-}MeC_3H_4)_2RhCl]_2$. 0.54 g (76%), m.p. 144—148°C (decomp.). Found: C, 38.63; H, 5.72. $C_{16}H_{28}Rh_2Cl_2$ calcd.: C, 38.66; H, 5.68%. IR spectrum: 3055, 3030, 2955, 2910, 2850, 1525, 1440, 1380, 1265, 1190, 1015, 975, 890, 840, 810, 555 cm^{-1}.

Bis(π-2-phenylallylrhodium chloride), $[(\pi\text{-}2\text{-}PhC_3H_4)_2RhCl]_2$. 0.9 g (81%), m.p. 165—170°C (decomp.). Found: C, 57.65; H, 4.91; Cl, 9.98; Rh, 27.71. $C_{36}H_{36}Rh_2Cl_2$ calcd.: C, 58.00; H, 4.87; Cl, 9.52, Rh, 27.62%. IR spectrum: 3060, 3030, 2990, 1605, 1585, 1480, 1465, 1375, 1345, 1315, 1190, 1165, 1085, 1035, 970, 910, 875, 845, 700, 640, 540, 515 cm^{-1}.

Bis(π-1-phenylallylrhodium chloride), $[(\pi\text{-}2\text{-}RhC_3H_4)_2RhCl]_2$. 0.8 g, (74%), m.p. 192—198°C (decomp.). Found: C, 57.71; H, 4.79. $C_{36}H_{36}Rh_2Cl_2$ calcd.: C, 58.00; H, 4.87%. IR spectrum: 3060, 3030, 2990, 2975, 2955, 2910, 2855, 1520, 1440, 1375, 1260, 1185, 1115, 1035, 1015, 1005, 915, 890, 803, 550 cm^{-1}.

Preparation of π-allyl-π-cyclopentadienylrhodium chlorides (general technique)

A finely ground mixture of 0.00949 mol of the allylmercury halide and 2.46 g (0.00949 mol) of C_5H_5Tl was added with stirring to a filtered solution of 2.50 g (0.00949 mol) of $RhCl_3 \cdot 3\ H_2O$ in 200 ml of a methanol/water mixture (5/1). The suspension was stirred for 6 h and filtered. The red filtrate was diluted with an equal amount of water and extracted with CH_2Cl_2. The extract was washed with water (2 × 50 ml), dried over $MgSO_4$ and evaporated on a rotor evaporator to a small volume. Addition of petroleum ether (m.p. 40—60°C) yielded complexes which were recrystallized from CH_2Cl_2/heptane (1/2). Using this method we prepared: π-Allyl-π-cyclopentadienylrhodium chloride, $\pi\text{-}C_3H_5Rh\text{-}\pi\text{-}C_5H_5(Cl)$. 0.8 g (40%), m.p. 175—183°C (decomp.). Found: C, 39.44; H, 4.49; Cl, 14.90. $C_8H_{10}RhCl$ calcd.: C, 39.30; H, 4.12; Cl, 14.50%. IR spectrum: 3100, 3030, 3010, 2950, 2880, 1485, 1465, 1400, 1550, 1235, 1215, 1110, 1020, 945, 910, 820, 795, 590, 575 cm^{-1}.

π-2-*p*-Fluorophenyl-π-cyclopentadienylrhodium chloride, $\pi\text{-}2\text{-}p\text{-}FC_6H_4C_3H_4\text{-}\pi\text{-}C_5H_5RhCl$. 1.1 g (35%), m.p. 183—187°C (decomp.). Found: C, 49.47; H, 3.86; Cl, 10.42. $C_{14}H_{13}RhClF$ calcd.: C, 49.70; H, 3.85; Cl, 10.47%. IR spectrum: 3085, 3020, 2930, 2860, 1620, 1590, 1485, 1440, 1410, 1570, 1270, 1220, 1175, 1080, 1025, 985, 950, 910, 880, 840, 810, 780, 725, 700, 665, 580, 540, 530, 510 cm^{-1}.

π-2-*m*-Fluorophenyl-π-cyclopentadienylrhodium chloride, $\pi\text{-}2\text{-}m\text{-}FC_6H_4C_3H_4$-

π-C_5H_5RhCl. 1.15 g (37%), m.p. 173—177°C (decomp.). Found: C, 49.57; H, 3.82; Cl, 10.65. $C_{14}H_{13}RhClF$ calcd.: C, 49.70, H, 3.85; Cl, 10.47%.

Preparation of π-methallyl-π-cyclopentadienyliridium halides

A solution of 0.00245 *M* of C_4H_7HgCl in 50 ml of CH_3OH was added to 0.00245 *M* of ($C_5H_5IrI_2$) in 100 ml of aqueous methanol (1/10); the mixture was stirred (20°C, 4 h), stored for 12 h and then filtered. The filtrate was poured into water and then extracted with benzene. The extract was washed with water, dried over $MgSO_4$, evaporated under vacuum to a small volume. Addition of petroleum ether and recrystallization from benzene/heptane (1/1) yielded 0.52 g (62%) of a yellow-orange adduct of composition $C_9H_{12}IrHgI_2Cl_2$, m.p. 248—250°C. Found: C, 13.33; H, 1.48; Hal, 36.35. $C_9H_{12}HgIrI_2Cl$ calcd.: C, 13.47; H, 1.51; Hal, 36.01%. On dissolution of the adduct in acetone and energetic agitation with a saturated aqueous solution of $Na_2S_2O_3$ the bright-orange color turned yellow and metallic mercury precipitated as a light-grey powder. The mixture was filtered and the filtrate extracted with benzene. The benzene extracts were twice washed with water, dried over $MgSO_4$ and evaporated under vacuum. The residue was dissolved in benzene and chromatographed on a thin layer of Al_2O_3 using benzene as eluant. The first eluate (R_f 0.56) gave (π-C_5H_5)(π-C_4H_7)IrI, m.p. 185—190°C. Found: C, 24.48; H, 2.85; I, 29.11. $C_9H_{12}IrI$ calcd.: C, 24.61; H, 2.74; I, 28.89%. IR spectrum (KBr): 3110, 3095, 3085, 2995, 2960, 1460, 1445, 1420, 1400, 1380, 1345, 1330, 110, 1050, 1010, 990, 890, 840, 825, 815, 605, 565 cm^{-1}.

The second eluate (R_f 0.15) yielded (π-C_5H_5)(π-C_4H_7)IrCl, m.p. 152—154°C. Found: C, 31.18; H, 3.41; Cl, 10.21. $C_9H_{12}IrCl$ calcd.: C, 31.08; H, 3.48; Cl, 10.19%. IR spectrum (KBr): 3100, 3065, 2995, 2960, 2930, 2860, 1445, 1405, 1385, 1350, 1105, 1005, 990, 970, 935, 900, 845, 610, 590 cm^{-1}.

Preparation of π-benzeneruthenium-π-allyl chlorides (general technique)

A solution of a 25% excess of the corresponding allylmercury chloride in 100 ml of methanol was added to 0.00224 moles of bis(π-benzeneruthenium chloride) in a mixture of 130 ml of methanol and 20 ml of water. The mixture was stirred under an inert atmosphere for 6 h, filtered, the filtrate diluted with water and extracted with CH_2Cl_2. The extract was dried over $MgSO_4$ and evaporated under vacuum. The residue was recrystallized from benzene/heptane (2/1). Using this technique we prepared: π-Allyl-π-benzeneruthenium chloride, π-C_3H_5-π-C_6H_6RuCl. 0.49 g (84%), m.p. 175—180°C (decomp.). Found: C, 42.43; H, 4.36. $C_9H_{11}ClRu$ calcd.: C, 42.27; H, 34%. NMR ($CDCl_3$): δ 2.27 ppm (2H, multiplet); 4.13 ppm (3H, multiplet); 5.51 ppm (6H, singlet). IR spectrum: 3060, 3020, 3005, 2940, 2920, 1480, 1440, 1390, 1230, 1210, 1140, 1020, 1005, 980, 900, 815, 800, 600 cm^{-1}.

π-Crotyl-π-benzeneruthenium chloride, π-1-MeC_3H_4-π-C_6H_6RuCl. 0.5 g (80%), m.p. 178—183°C (decomp.). Found: C, 44.33; H, 4.65; Cl, 13.54. $C_{10}H_{13}RuCl$ calcd.: C, 44.53; H, 4.81; Cl, 13.14%. IR spectrum: 3060, 3010, 2965, 2860, 1460, 1445, 1420, 1350, 1235, 1200, 1155, 1140, 1040, 980, 935, 885, 860, 815, 780, 615, 530, 500 cm^{-1}.

π-Methallyl-π-benzeneruthenium chloride, π-2-MeC_3H_4-π-C_6H_6RuCl. 0.42 g (70%), m.p. 205—212°C (decomp.). Found: C, 43.92; H, 4.62. $C_{10}H_{13}RuCl$

calcd.: C, 44.53; H, 4.81%. NMR ($CDCl_3$): δ 1.51 ppm (3H, singlet); 2.27 ppm (2H, singlet); 4.13 ppm (2H, singlet); 5.49 ppm (6H, singlet). IR spectrum: 3060, 2990, 2960, 2920, 1615, 1440, 1380, 1335, 1145, 1050, 1035, 1025, 1000, 780, 965, 935, 905, 850, 810, 615, 590 cm^{-1}.

π-2-Phenylallyl-π-benzeneruthenium chloride, π-2-PhC_3H_4-π-C_6H_6RuCl. 0.43 g (58%), m.p. 174—177°C (decomp.). Found: C, 54.39; H, 4.53. $C_{15}H_{15}$-RuCl calcd.: C, 54.30; H, 4.56%. IR spectrum: 3055, 3000, 2920, 1510, 1475, 1435, 1360, 1160, 1083, 1035, 1020, 1005, 975, 035, 905, 825, 805, 785, 760, 660, 590, 560, 545, 500 cm^{-1}.

π-1-Phenylallyl-π-benzeneruthenium chloride, π-1-PhC_3H_4-π-C_6H_6RuCl. 0.46 g (62%), m.p. 176—178°C (decomp.). Found: C, 54.00; H, 4.50. $C_{15}H_{15}RuCl$ calcd.: C, 54.30; H, 4.56%. IR spectrum: 3065, 3025, 3000, 1600, 1520, 1490, 1435, 1385, 1335, 1285, 1250, 1210, 1180, 1140, 1080, 1045, 1020, 1005, 995, 975, 325, 880, 820, 785, 765, 705, 610, 575, 540 cm^{-1}.

π-1-Acetyl-2-methylallyl-π-benzeneruthenium chloride, π-1-MeCO-2-MeC_3H_3-π-C_6H_6RuCl. 0.4 g (57%), m.p. 187—191°C (decomp.). Found: C, 46.22; H, 4.81; Cl, 11.33. $C_{12}H_{15}RuClO$ calcd.: C, 46.23; H, 4.85; Cl, 11.37%. IR spectrum: 3065, 3035, 3015, 2990, 2965, 1665, 1480, 1385, 1360, 1300, 1180, 1045, 1025, 1000, 970, 925, 915, 980, 890, 820, 790, 630, 610, 575 cm^{-1}.

Interaction of π-benzeneosmium chloride with allylmercury compounds

A solution of 0.0028 mol of the allylmercury compound in 50 ml of methanol was added under argon atmosphere to a light-red solution of 0.94 g (0.0028 mol) of π-benzeneosmium dichloride in a mixture of 150 ml of methanol and 10 ml of water. The reaction mixture was stirred at room temperature for 5 h and then filtered. The filtrate was diluted with water, extracted with benzene; the benzene extract was washed twice, dried over $MgSO_4$ and evaporated to a small volume. On addition of light petroleum ether a yellow-green substance precipitated which was recrystallized from benzene/heptane (1/1). Using this method we prepared: π-Benzene-π-allylosmium chloride, π-C_6H_6OsCl-π-C_3H_5. 0.53 g (52%), m.p. 188—194°C (decomp.). Found: C, 31.59; H, 3.41. $C_9H_{11}ClOs$ calcd.: C, 31.35; H, 3.21%. IR spectrum: 3065, 2995, 1470, 1430, 1980, 1220, 1190, 1135, 1015, 995, 980, 940, 910, 820 cm^{-1}. NMR spectrum ($CDCl_3$): 5.53 ppm (6H, singlet); 4.82 ppm (1H, multiplet); 4.30 (2H, doublet, J 5.5 Hz); 2.10 (2H, doublet, J 12 Hz).

π-Benzene-π-methallylosmium chloride, π-C_6H_6OsCl-π-C_4H_7. 0.55 g, m.p. 225—228°C (decomp.). Found: C, 33.20; H, 3.85; Cl, 10.09. $C_{10}H_{13}ClOs$ calcd.: C, 33.47; H, 3.65; Cl, 9.88%. IR spectrum: 3080, 3060, 2995, 2925, 1425, 1380, 1360, 1380, 1145, 1040, 1020, 990, 980, 970, 960, 925, 855, 825 cm^{-1}.

Preparation of π-allylbis(triphenylphosphine)platinum chlorides (general technique)

A colorless solution of 0.0004 mol of allylmercury halide in 20 ml of benzene was added under argon atmosphere to an orange-yellow solution of 0.0004 mol $(PPh_3)_4Pt$ in 50 ml of benzene. After 5 min the solution became colorless and a grey Hg precipitate was formed. The mixture was stirred for another hour, filtered and the filtrate was diluted with ether to complete precipitation of the reaction product, which was filtered, thoroughly washed with ether to remove PPh_3 and dried under reduced pressure. The white substance was then recrystallized. Using this method we obtained: Bis(triphenylphosphine)-π-allylplatinum chloride, $(PPh_3)_2Pt(C_3H_5)Cl$. 0.2 g (70%), decomp. 194—198°C. Found: C, 58.51; H, 4.36; Cl, 4.90. $C_{39}H_{35}PtP_2Cl$ calcd.: C, 58.83; H, 4.43; Cl, 4.45%. IR spectrum: 3080, 3050, 1005, 945, 930, 870, 850, 760, 730, 700, 545, 510 cm^{-1}. PMR spectrum ($CHCl_3$) δ 3.56 (unresolved signal, 4H), 6.10 ppm (m, 1H).

Bis(triphenylphosphine)-π-2-phenylallylplatinum chloride, $(PPh_3)_2Pt(C_6H_9)Cl \cdot CHCl_3$. 0.22 g (70%), decomp. 287—293°C. Found: C, 55.39; H, 3.94; Cl, 14.00; P, 6.80. $C_{43}H_{40}PtP_2Cl_4$ calcd.: C, 55.71; H, 4.06; Cl, 14.30; P, 6.25%.

Bis(triphenylphosphine)-π-acetyl-2-methylallylplatinum chloride, $(PPh_3)_2Pt(C_6H_9O)Cl \cdot CHCl_3$. 0.16 g (54%), decomp. 295—300°C. Found: C, 53.14;

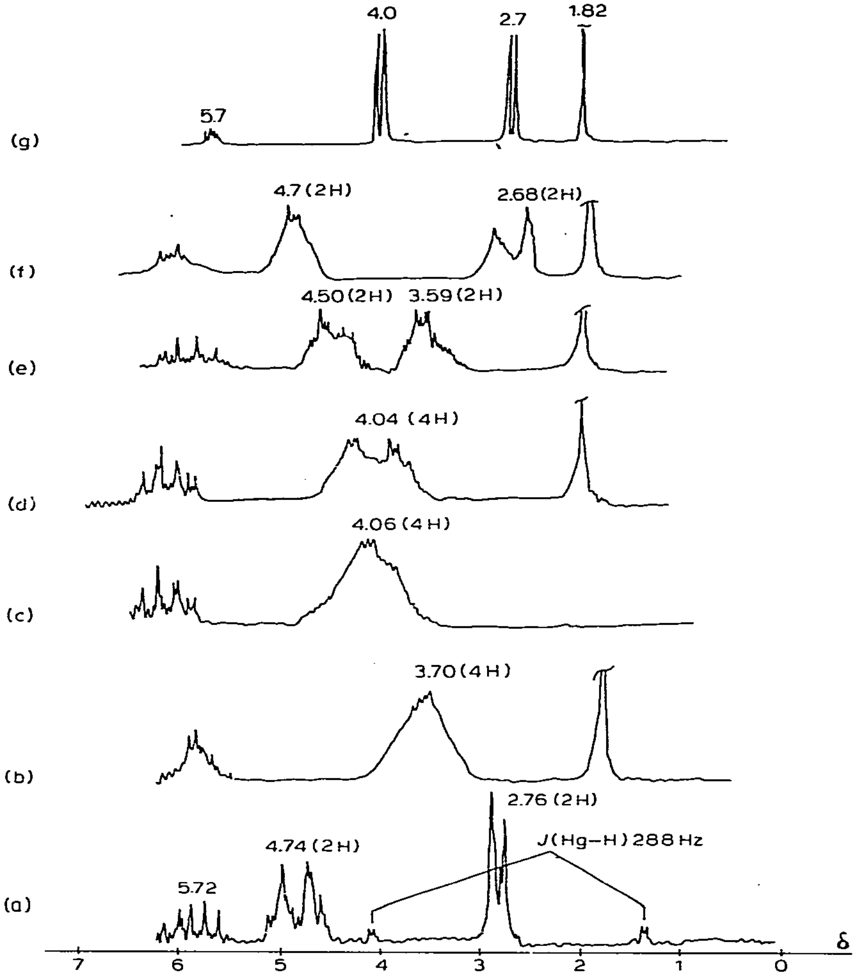


Fig. 1. Interaction of allylmercury chloride with palladium acetate: (a) allylmercury chloride ($CDCl_3$, 25°C); (b) allylmercury chloride + equimolecular quantity of $Pd(OAc)_2$; (c) allylmercury chloride + catalytic amount of $HgCl_2$; (d—f) allylmercury chloride + catalytic amount of $HgCl_2$ + equimolecular amount of $Pd(OAc)_2$ after 1, 4 and 24 h; (g) π-allylpalladium acetate ($CDCl_3$, 25°C).

H, 3.92; Cl, 14.02; P, 6.20. $C_{43}H_{40}PtP_2Cl_4O$ calcd.: C, 53.15; H, 4.15; Cl, 14.58; P, 6.28%. IR spectrum: 3080, 3060, 3030, 3010, 2990, 1680, 1650, 1590, 1580, 1485, 1435, 1315, 1195, 1165, 1100, 1035, 760 700, 620, 555, 535, 520, 505 cm^{-1}.

Bis(triphenylphosphine)-π-1-methylallylplatinum chloride, $(PPh_3)_2Pt(C_4H_7)Cl \cdot CHCl_3$. 0.22 g, (70%), m.p. 268—274°C (decomp.). Found: C, 52.85; H, 3.79; Cl, 14.98; P, 6.33. $C_{41}H_{38}PtP_2Cl_4$ calcd.: C, 52.97; H, 4.12; Cl, 15.25; P, 6.66%.

Bis(triphenylphosphine)-π-2-methylallylplatinum chloride, $(PPh_3)_2Pt(C_4H_7)Cl \cdot CHCl_3$. 0.2 g (65%), 290—295°C (decomp.). Found: C, 52.81; H, 3.94; Cl, 15.10; P, 6.28. $C_{41}H_{38}PtCl_4P_2$ calcd.: C, 52.97; H, 4.12; Cl, 15.25; P, 6.66%.

Interaction of platinum(II) and platinum(IV) compounds with allylmercury chloride (general technique)

A solution of 0.003 mol of allylmercury chloride in 50 ml of CH_3OH was added under argon atmosphere to 0.003 mol of Pt compound in 100 ml of CH_3OH at ~20°C. The mixture was stirred for 3—4 h and filtered. The filtrate was diluted with water and extracted with chloroform. The aqueous layer was evaporated and the residue was analyzed for Hg^{2+} and Hg^{+} by addition of NaOH.

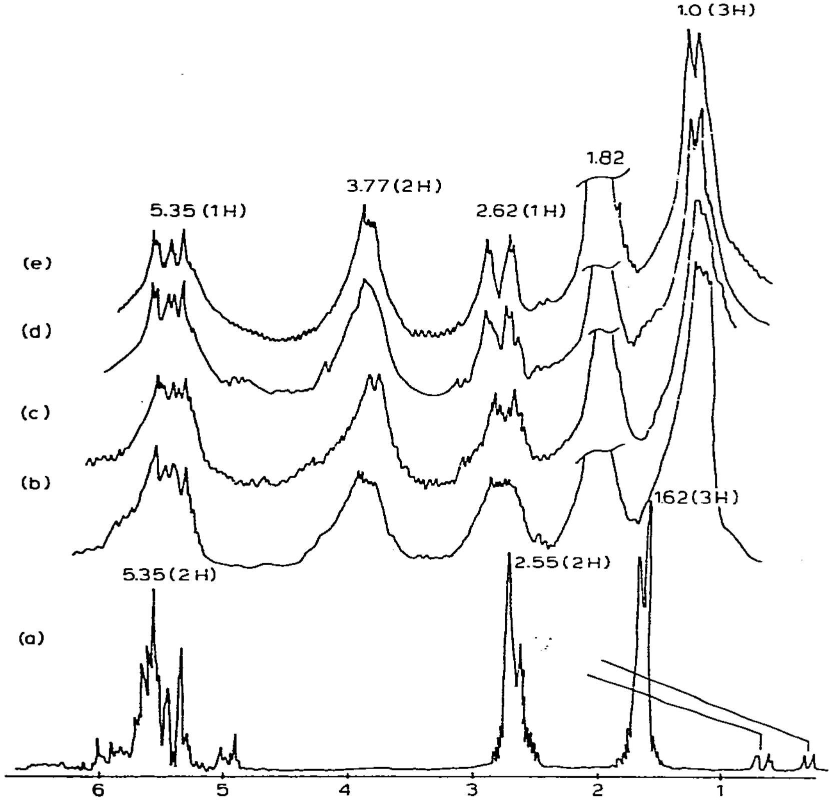


Fig. 2. Interaction of crotylmercury chloride with palladium acetate: (a) crotylmercury chloride ($CDCl_3$, 25°C); (b) $C_4H_7HgCl + Pd(OAc)_2$ (1/1) 10 min after mixing; (c—e) after every 0.5 h.

The organic layer was also evaporated and the condensate was collected in a cooled (—78°C) receiver. After removing the solvent the residue was recrystallized and analyzed. The condensate was analyzed by GLC for the presence of diallyl.

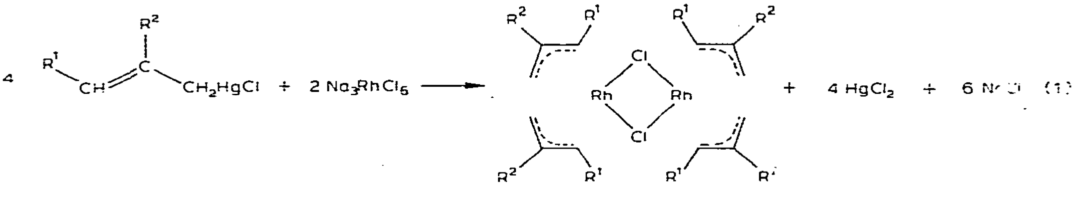
PMR study of the interaction of $Pd(OCOCH_3)_2$ with allylmercury compounds

A weighted sample of an allylmercury compound was dissolved in an appropriate solvent and the PMR spectrum was recorded. A solution of an equivalent amount of $Pd(OCOCH_3)_2$ in the same solvent was added to the ampoule and the spectra were then recorded every 30 min. Results obtained for allyl- and crotylmercury chlorides are shown in Fig. 1 and 2. Figure 1c—1e presents data of the $Pd(OCOCH_3)_2$ allylmercury chloride reaction in the presence of a catalytic amount of mercuric chloride.

Results and discussion

Synthesis of π-allyl compounds of rhodium and iridium

After addition of a methanol solution of the allylmercury derivative to a water/methanol solution of Na_3RhCl_6 the color changed from the original cherry-red to yellow usually in 10—12 h at 20°C. Bis(allylrhodium) complexes were isolated from the reaction mixture.



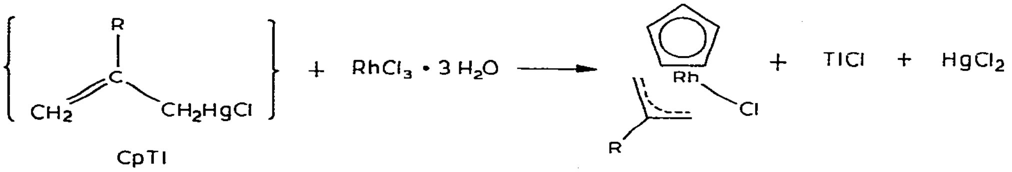
(I)

The structure of complexes I was established on the basis of IR and PMR spectra and chemical conversions. The complexes described in the present work enter into reactions typical of π-allylrhodium complexes [15]. For instance, I ($R^1 = R^2 = H$) reacts with C_5H_5Tl to form π-cyclopentadienyl-π-allyl-σ-allylrhodium, the interaction of which with an alcohol solution of HCl results in the rupture of the C—Rh σ-bond and formation of π-cyclopentadienyl-π-allylrhodium chloride (II). Tris-allylrhodium was obtained by reaction of I ($R^1 = R^2 = H$) with allylmagnesium chloride in ether. The structure of the complexes was established from the IR spectra.

The proposed method of synthesis of π-allylrhodium derivatives, while having yields which are not worse than those obtained by known methods, has several advantages. Firstly, the initial compound is the readily available rhodium(III) chloride and secondly, a larger number of substituted complexes may be obtained by this method, since substituted allylmercury compounds are easily obtained by the reaction of π—σ transfer of the allyl ligand from Pd to the Hg atom [5].

We have also proposed a new one-step method for preparation of II, which consists of simultaneous allylation and cyclopentadienylation of $RhCl_3 \cdot 3\,H_2O$

by allylmercury halides and thallium cyclopentadienide. The reaction occurs in



(2)

(II)

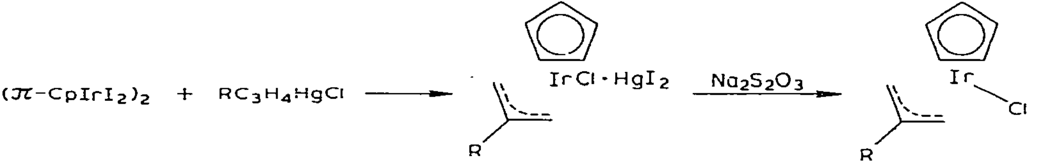
aqueous methanol at ~20°C and proceeds to completion in 5—6 h. The yields of II are 30—35% in $RhCl_3 \cdot 3\ H_2O$.

The synthesized compounds were characterized by elemental analysis and IR spectroscopy; their structure was proved by independent synthesis and comparison of IR spectra with those of authentic samples.

Compounds II may be formed by two different routes. The first route involves intermediate formation of dimeric bis(π-allylrhodium) chloride, which then reacts with C_5H_5Tl yielding a σ-allyl derivative. But since mercuric chloride is formed in the reaction, the rhodium—allyl σ-bond is ruptured and under the action of $HgCl_2$ leading to formation of II and possibly of allylmercury chloride. However, all attempts to establish the latter in the products of reaction 2 failed. It was also established by a separate experiment that $RhCl_3 \cdot 3\ H_2O$ does not undergo allylation in the presence of allylmercury chloride.

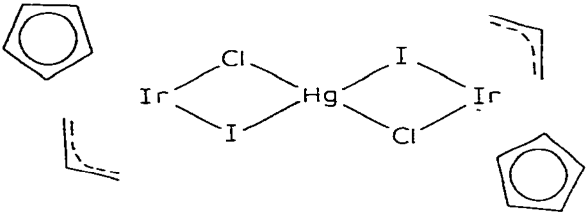
The second route involves intermediate formation of allylcyclopentadienylmercury as a result of interaction of C_5H_5Tl with C_2H_5HgCl. It is known [16] that C_5H_5Tl may cyclopentadienylate mercuric chloride with formation of dicyclopentadienylmercury. The unstable intermediate $C_5H_5HgC_3H_5$ then reacts with $RhCl_3$ according to a S_E1 or S_Ei mechanism [17] with formation of II. The absence of conclusive experimental evidence does not allow us to make a final choice, although unsuccessful attempts to establish allylmercury chloride among the reaction products favours the second route.

The π-allyl-π-cyclopentadienyl iridium compounds obtained in this work were previously unknown.



(3)

Unlike other allylation reactions of platinum metals using allylmercury chloride, the source of halogen in our reaction in the π-allyl complex is C_3H_5HgCl and not the platinum metal derivative. Possibly "halogen exchange" occurs during reduction of the intermediate adduct with the mercury salt (π-C_5H_5)-(π-C_3H_5)$IrHgI_2Cl$ by sodium thiosulfate. The precise structure of the adduct has not yet been determined, but by analogy with literature data [19] a dimer with halogen bridges may be assumed:



Evidently, the Ir—I bond is more easily ruptured in the presence of $Na_2S_2O_3$.

Interaction of 2-methallylmercury chloride with $(\pi\text{-}C_5H_5IrI_2)_2$ also leads to an adduct of similar composition, $(\pi\text{-}C_5H_5)(\pi\text{-}C_3H_4CH_3)IrHgI_2Cl$, but reduction of the latter with $Na_2S_2O_3$ results in the formation of two complexes, π-methallyl-π-cyclopentadienyliridium chloride (III) and iodide (IV) in a 8/1 ratio. These compounds were separated by TLC on Al_2O_3 in benzene and characterized by elemental analysis and PMR and IR spectra.

According to the PMR spectra both complexes have the π-methallyl-π-cyclopentadienyl structure (Fig. 3a, b); the observed differences in chemical shifts of *syn* and *anti* protons of the π-methallyl ligand in the chloride and iodide ($\Delta\delta_{syn}$ 0.20 ppm upfield; $\Delta\delta_{anti}$ 0.66 ppm downfield) are typical of π-allyl complexes when chlorine is displaced by iodine [20]. The IR and Raman spectra of these complexes both in crystalline form and in solution differ considerably in the regions of stretching and bending vibrations of C—H bonds of the π-C_5H_5 ligand: the iodide displays a much more complex pattern than the chloride. Presumably these complexes have some intricate differences in the structure which are not reflected in the NMR spectra, but affect vibrational transitions in the molecule.

To determine these differences we carried out an X-ray diffraction study of these compounds.

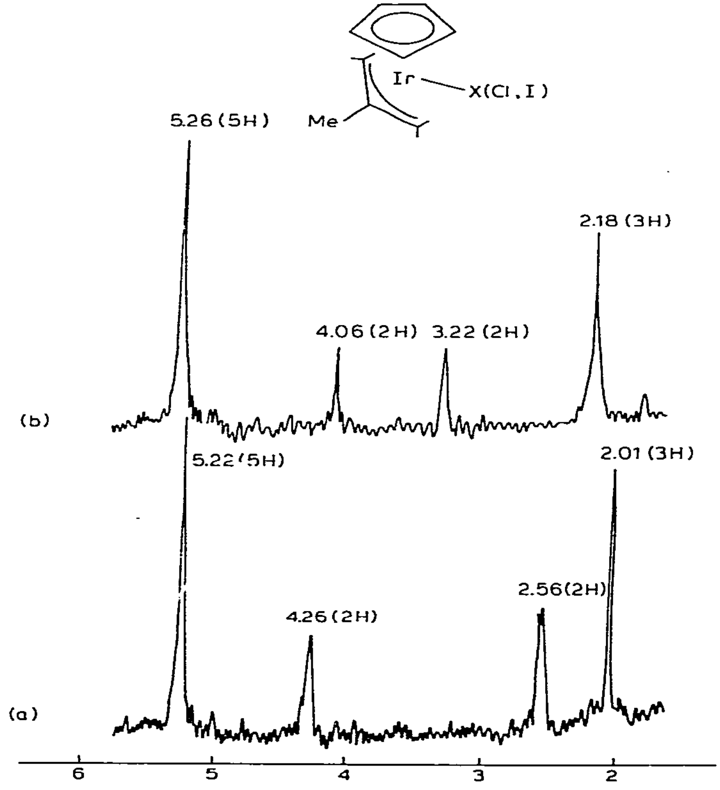
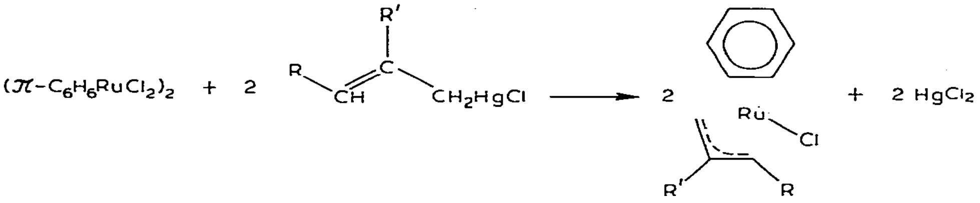


Fig. 3. PMR spectra of π-cyclopentadienyl-π-methallyliridium chloride (a) and iodide (b) ($CDCl_3$, 25° C).

Molecules in crystals of III and IV have similar structures (Fig. 4a, b). In both molecules the Ir—X and C(2)—C(4) bonds (in the allyl ligand) are almost coplanar. However, while in the molecule of III this plane practically coincides with the noncrystallographic plane of symmetry (Fig. 4a, b), in molecule IV this symmetry is distorted by the Cp-ligand turning in its own plane by an angle of 26°. This rotation may be due to the trend to decrease the covalent Ir ··· C(7) distance, although the barrier to this rotation can hardly be large enough for II and IV to be rotation isomers. Due to the displacement of the Cp ligand, the symmetry in IV is lowered as compared with III. This may account for the more complex vibrational spectrum of IV.

Synthesis of π-allyl-rhuthenium and -osmium compounds

Dimeric π-benzeneruthenium dichloride, $[(\pi\text{-}C_6H_6)RuCl_2]_2$, was used as the starting compound in the study of allylation of ruthenium halides. This compound is readily soluble in methanol and acetonitrile, evidently, with formation of monomeric species of the type $[\pi\text{-}C_6H_6RuCl \cdot solv]$, which are very reactive [21]. It was established that they react with allylmercury compounds under mild conditions forming π-benzeneruthenium-π-allyl chlorides:



(4)

R = R' = H ; R = Me , R' = H
R = H , R' = Me ; R = Ph , R' = H
R = H , R' = Ph ; R = Ac , R' = Me

In the case of allyl- and crotyl-mercury chlorides reactions in acetonitrile give yellow crystalline substances, which are poorly soluble in organic solvents. According to elemental analysis these compounds correspond to the composition $C_6H_6Ru(allyl) \cdot HgCl_3 \cdot MeCN$; the presence of coordinated acetonitrile in the molecule is indicated by absorption at 2130 cm^{-1} in the IR spectra, corresponding to stretching vibrations of the nitrile group coordinated with a metal atom [22].

All compounds were characterized by IR and PMR spectra. The PMR spectrum of π-benzeneruthenium-π-allyl chloride displays a sharp signal at δ 5.51 ppm belonging to the protons of the π-benzene ligand (6H) and two multiplets at δ 4.3 and 2.27 ppm with an intensity ratio of 4/1 from the central and terminal *syn* and *anti* protons of the π-allyl ligand [23]. A more simple spectrum was observed in the case of π-benzene-π-methallylruthenium chloride, showing four signals at δ 5.49, 4.13, 2.27 and 1.51 ppm with an intensity ratio of 6/2/2/3. The signals at δ 5.49 and 1.51 ppm are displayed by protons of the π-benzene ligand and the methyl group respectively; signals at δ 4.13 and 2.27 ppm correspond to terminal *anti* and *syn* protons of the π-methallyl ligand.

Osmium analogues of π-benzeneruthenium-π-allyl chloride were synthesized

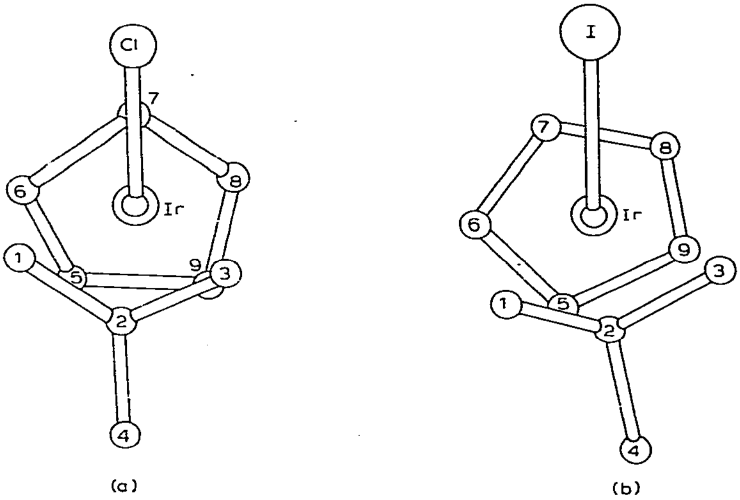
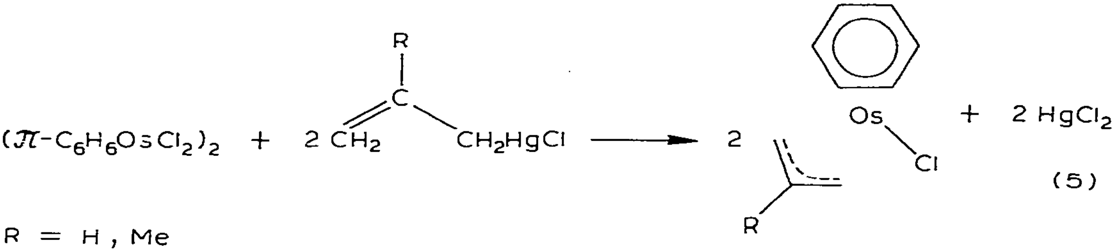


Fig. 4. Projections of π-$C_5H_5Ir(Cl)$-π-C_4H_7 (a) and π-$C_5H_5Ir(I)$-π-C_4H_7 (b) molecules on the plane of Cp rings.

by interaction of bis(π-benzene-osmium chloride) with allylmercury compounds:

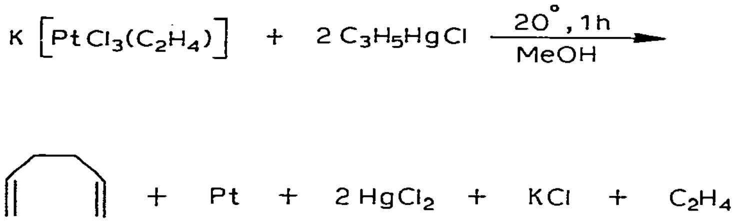


(5)

The reaction is carried out in aqueous methanol at room temperature for 5—6 hours; π-allylosmium complexes are formed in yields exceeding 50% as yellow-green crystalline substances stable in air. The structure of the compounds was established on the basis of IR and PMR spectra. IR spectra of osmium complexes in the 3500—700 cm^{-1} region are similar to those of ruthenium derivatives: they display bands at 1470, 1220, 1015 and 820 cm^{-1} typical of the coordinated π-allyl ligand [24] and bands at 3065, 1430, 995 and 820 cm^{-1} characteristic of a π-bonded benzene ring [25]. The PMR spectra of all compounds show a narrow singlet at δ 5.53 ppm from the six equivalent protons of the π-bonded benzene ring. In the region of the π-allyl protons the NMR spectrum of π-$C_6H_6Os(Cl)$-π-C_3H_5 is much better resolved than the spectrum of π-$C_6H_6Ru(Cl)$-π-C_3H_5. At 30°C the spectrum exhibits well resolved lines corresponding to a A_2B_2X spin system, typical of a π-allyl group [15]. Apparently dynamic rearrangements of the π-allyl ligand are hindered in the case of the osmium complex as compared with the ruthenium analogue. Such hindrance of exchange processes in the π-allyl ligand with increase of the atomic number of the central atom has been mentioned in ref. 26.

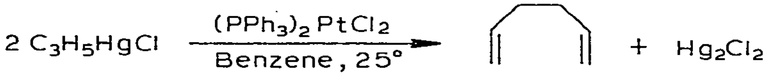
Interaction of allylmercury halides with platinum and palladium compounds

Platinum(IV) and platinum(II) compounds may be divided into two groups according to the character of their reactions with $CH_2{=}CHCH_2HgCl$. The first group includes compounds of the type M_2PtCl_6 and M_2PtCl_4 (M = K, Na), Zeise salt $K[PtCl_3(C_2H_4)]$ and its dimer $(C_2H_4PtCl_2)_2$. These platinum(II) and platinum(IV) derivatives react with allylmercury chloride forming platinum and mercury(II) salts and diallyl, for example:



(6)

The second group of compounds includes complexes of the type L_2PtX_4 and L_2PtX_2, where L = PhCN or PPh_3. These platinum(II) and platinum(IV) derivatives react with C_3H_5HgCl forming diallyl and mercury(I) salt. The starting Pt compound does not change during the reaction, for instance:



(7)

This process may be due to the presence of free PPh_3 ligand, which may act as a symmetrization agent. Diallylmercury formed during symmetrization decomposes under reaction conditions with formation of diallyl and Hg, the latter reacting with mercuric chloride to give calomel:

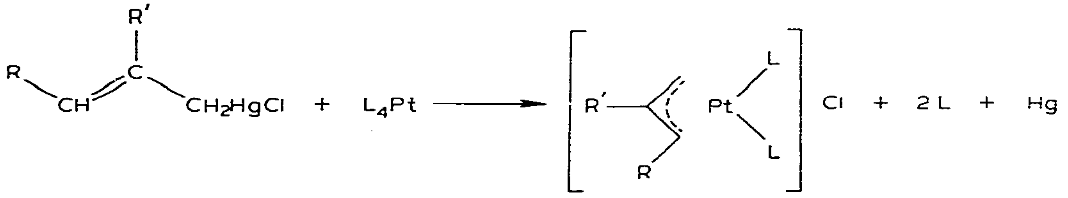
$$2\,C_3H_5HgCl \rightarrow C_3H_5\text{-}Hg\text{-}C_3H_5 + HgCl_2 \tag{8}$$

$$C_3H_5HgC_3H_5 \rightarrow C_3H_5\text{-}C_3H_5 + Hg \tag{9}$$

$$HgCl_2 + Hg \rightarrow Hg_2Cl_2 \tag{10}$$

In several cases we were able to isolate Hg.

L_4Pt (L = PPh_3) instantly reacts with allylmercury halides in benzene at ~20°C. After evaporation of the reaction mixture π-allyl cationic complexes were obtained:



(11)

R = R' = H ; R = H, R' = Me ; R = H, R' = Ph; R = Me, R' = H; R = Ph, R' = H ;

R = Ac, R' = Me

Under similar conditions alkyl and phenyl derivatives of mercury(II) form σ-complexes, $(PPh_3)_2PtR(X)$ (R = alkyl, aryl), in reactions with $(PPh_3)_4Pt$ [27].

The π-allyl complexes are white stable compounds, poorly soluble in organic solvents and soluble only in chloroform forming 1/1 adducts with the solvent.

Although the proposed synthesis of π-allylbis(triphenylphosphine) complexes of platinum (at least, for π-allylbis(triphenylphosphine)platinum chloride) is less convenient than the reaction of L_4Pt with allyl halides, the latter method cannot be used to prepare a wide range of substituted π-allyl complexes (for instance 2-phenyl or 1-acetyl-2-methyl derivatives) as the corresponding substituted allyl halides are inaccessible.

The effect of various factors on the reaction was studied for the allylation of palladium compounds by allylmercury compounds. It was established that the relative rates of process 12 and the yields of the end-products to a considerable extent depend on the spatial-electronic environment at the double bond of the allylmercury compound and on the nature of the anion X bonded to the palladium atom. We obtained the following series of reactivity of the allylmercury chlorides: allyl = $CH_2{=}CHCH_2$ > ($MeCH{=}CHCH_2$, $PhCH{=}CHCH_2$, $CH_2{=}C(Me)CH_2$, $CH_2{=}C(Ph)CH_2$) > $MeCOCH{=}C(Me)CH_2$ >> $CH_2{=}C(neo\text{-}C_5H_{11})CH_2$. As can be seen from this series, an inverse in the steric hindrance and the electron density of the double bond sharply reduces the capacity of mercury compounds to allylate palladium salts. For instance, $CH_2{=}C(neo\text{-}C_5H_{11})CH_2HgCl$ practically does not form π-allylpalladium complexes, $MeCOCH{=}C(Me)CH_2HgCl$ reacts with formation of the corresponding π-allyl compound over a period of 0.5 h, unsubstituted allylmercury chloride gives in quantitative yields bis-π-allylpalladium chloride after stirring with Na_2PdCl_4 (for 2—3 min).

$$2\ RC_3H_4HgX + 2\ PdX_2 \rightarrow (RC_3H_4PdX)_2 + 2\ HgClX \qquad (12)$$

The nature of the anion X affects not only the reaction rate Br > Cl > CH_3COO but also the composition of the products formed:

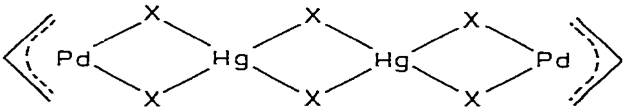
$$K_2PdCl_4 + 2\ C_3H_5HgCl \rightarrow (C_3H_5PdCl \cdot HgCl_2)_2 \rightarrow (C_3H_5PdCl)_2 \qquad (13)$$

$$K_2PdBr_4 + 2\ C_3H_5HgCl \rightarrow (C_3H_5PdBr \cdot HgClBr)_2 \rightarrow (C_3H_5PdBr)_2 + HgClBr \qquad (14)$$

$$Pd(OCOCH_3)_2 + C_3H_5HgCl \rightarrow (C_3H_5PdOCOCH_3)_2 + Hg(Cl)OCOCH_3 \qquad (15)$$

$$K_2PdCl_4 + 2\ C_3H_5HgBr \rightarrow (C_3H_5PdCl \cdot HgClBr)_2 \rightarrow (C_3H_5PdCl)_2 + HgClBr \qquad (16)$$

In the case of palladium chlorides and bromides formation of 1/1 adducts of π-allyl complexes with mercury(II) salts was observed. Palladium acetate does not form such mercury-containing derivatives. The π-allylpalladium halide adducts are not very stable: the HgX_2 molecule is easily eliminated even during recrystallization. According to IR and NMR data these adducts are π-allylpalladium complexes with mixed palladium and mercury-halide bridges.



It should be noted that addition of HgX_2 to bis-π-allyl-palladium halide complexes and prolonged mixing does not lead to formation of adducts, and, as can be seen from the equations, the source of the bridging group in the end π-allyl complex is always the initial palladium salt.

Therefore, it may be concluded that both the double bond of the allyl compound and the anionic fragment of the molecule attacking the palladium-containing reagent participate in allylation of palladium salts. Nucleophilic assistance of the anion bonded to palladium is clearly observed. The effect of the anion is directly related to its capacity to coordinate with the mercury atom [28]. The series of anion influence on the relative rates of the reaction obtained in the present work (Br > Cl > CH_3COO) point to a considerable contribution of nucleophilic coordination. From this point of view there is great similarity between palladium salt allylation and reactions of single alkyl exchange between allylmercury halides and inorganic mercury salts. The mechanism of the latter process was studied in detail by Winstein et al. [17,29]. They established that these reactions proceed as intramolecular electrophilic substitutions with a closed transition state and allyl rearrangement (S_Ei mechanism). It may be assumed that allylation of palladium salts by allylmercury halides proceeds in the same manner. To verify this assumption we investigated interaction of allylmercury chloride with palladium acetate by NMR spectroscopy.

The NMR spectrum of allylmercury chloride (Fig. 1a) displays a doublet at δ 2.76 ppm (2H), a triplet at 4.74 ppm (2H) and a complex multiplet at δ 5.72 ppm (1H), additionally several satellite signals were observed due to $^{199}Hg—^1H$ spin—spin coupling ($J(^{199}Hg—^1H)$ 288 Hz). Therefore it may be assumed that under these conditions (acetone-d_6, room temperature) allylmercury chloride is a covalent σ-allyl compound, which does not undergo any exchange processes with rupture of the C—Hg * σ-bond. Addition of equimolecular quantities of palladium acetate into the NMR ampoule containing allylmercury chloride leads to a sharp change of the spectrum (Fig. 1b), disappearance of satellites indicates rapid cleavage of the C—Hg σ-bond. The appearance of a wide resonance signal at σ 3.70 ppm, i.e. precisely between signals of $—CH_2$ and $=CH_2$ protons points to rapid exchange between these protons. Similar changes occur in the NMR spectrum of allylmercury chloride after addition of catalytic quantities of mercuric chloride (Fig. 1c). It has been reported that in the presence of mercuric chloride allylmercury chloride undergoes an exchange reaction which follows the mechanism of electrophilic intramolecular substitution with the formation of a closed six-centered transition state; the exchange rate is characterized by a rate constant $k = 10^{-3}$ sec^{-1}, i.e. vinyl and methylene protons change their environment 1000 times in a second. Results obtained during the study of the isotopic exchange of mercury between $^{203}HgCl_2$ and allylmercury chloride [29] indicate that this reaction is one of the fastest exchange reactions known for organomercurials.

Introduction of substituents into the γ-position of the allyl system [30] strongly hinders isotopic exchange: for cinnamylmercury bromide (eq. 17)

$$C_6H_5CH{=}CHCH_2HgBr + {}^{203}HgBr_2 \rightarrow C_6H_5CH{=}CHCH_2\,{}^{203}HgBr + HgBr_2 \qquad (17)$$

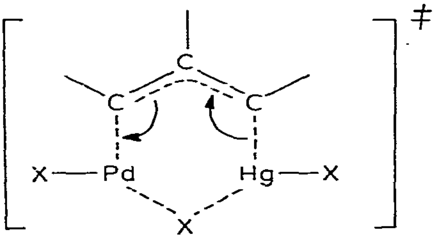
equilibrium sets in approximately after 5 h [30]; for crotylmercury bromide

---

* This conclusion does not conform with findings of Kitching et al. [29], who on the basis of NMR data concluded that allylmercury chloride, like allylmagnesium derivatives, is in a dynamic state due to rapid allyl rearrangement in the NMR time scale. Evidently the samples of allylmercury chloride used by these authors contained an admixture of mercuric chloride, in the presence of which a fast allyl rearrangement indeed does take place. Samples of C_3H_5HgCl used in our study were synthesized according to the method described in ref. 5 which excludes formation of mercury(II) salts.

the presence of mercury bromide does not enhance allyl rearrangement [29]. It is considered [29] that this effect of the substituent on the reaction of single alkyl exchange in allylmercury compounds is due to the fact that the formation of α-substituted allylmercury halides is not typical and that these compounds are unstable, and the equilibrium is practically completely displaced towards the initial γ-substituents. In the case of allylation of palladium resulting in formation of π-allyl complexes this thermodynamic factor should not be very important. Indeed, it was established that in the system crotylmercury chloride/ palladium acetate (Fig. 2) transfer of the allyl group from mercury to palladium proceeds with about the same rate as in the system $C_3H_5HgCl/Pd(OCOCH_3)_2$. Practically immediately after mixing the reagents the NMR spectrum of the initial crotylmercury chloride (Fig. 2a) changes, and the obtained spectral pattern (Fig. 2b) indicates rapid exchange between vinyl and methylene protons (the signal at δ 3.77 ppm is approximately in the middle between the signals from CH_2— and =CH protons). Further changes in the NMR spectra (Fig. 1c, d) occur more slowly.

Therefore, from the results obtained in this work it may be concluded that allylation of palladium salts by allylmercury chloride follows the same mechanism as allyl rearrangement of allylmercury salts in the presence of inorganic mercury salts. However, the transition state of the allylation reaction differs from the transition state in the exchange reaction in the system $C_3H_5HgCl/HgCl_2$ first of all in symmetry and also in the distribution of electronic density in the six-membered cycle. The PdX moiety bonded to the allyl system is known to have a much stronger electron-withdrawing capacity than the HgX group [31]. Consequently, in the transition state electronic displacements will occur mainly in the following manner:



In other words, unlike exchange in the system allylmercury chloride/mercuric chloride, allylation of palladium salts by allylmercury compounds should be irreversible. Indeed, addition of palladium acetate to the dynamic equilibrium system $C_3H_5HgCl/HgCl_2$ (Fig. 1d, e) leads to a constant change of the AX_4 spin system into a A_2B_2X system which is typical of the end π-allylpalladium acetate (Fig. 1f). In their turn, mercuric chloride and mercury acetate do not induce any exchange processes in bis-π-allylpalladium chloride (NMR data).

Therefore, on the basis of the results obtained in this work it may be assumed that allylation of palladium salts by allylmercury compounds proceeds as intramolecular electrophilic substitution with the formation of a closed six-centered transition state. The electrophilic nature of the reaction is slightly increased compared with a similar process in the system allylmercury chloride/mercuric chloride on account of higher electron-withdrawing requirements of the palladium acetate fragment in relation to the similar mercury-containing group.

Acknowledgement

The authors are grateful to Drs. Yu.T. Struchkov, T.N. Salnikova and V.G. Andrianov for interpreting the X-ray diffraction patterns and to Dr. P.V. Petrovsky for recording and discussing the NMR spectra.

References

1 M.I. Lobach, B.D. Babitsky and V.A. Kormer, Usp. Khim., 36 (1976) 1158.
2 E.W. Abel and S. Moorhouse, J. Chem. Soc. Dalton Trans., (1973) 1706.
3 T. Abel, H. Kurasawa and R. Okawara, J. Organometal. Chem., 25 (1970) 353.
4 J.M. Kliegman, J. Organometal. Chem., 29 (1971) 73.
5 A.N. Nesmeyanov, A.Z. Rubezhov, L.A. Leites and S.P. Gubin, J. Organometal. Chem., 12 (1968) 187.
6 A.N. Nesmeyanov, A.Z. Rubezhov, S.P. Gubin, A.S. Ivanov and L.I. Voronchikhina, Izv. Akad. Nauk SSSR, Ser. Khim., (1971) 2359.
7 A.Z. Rubezhov, A.S. Ivanov and S.P. Gubin, Izv. Akad. Nauk SSSR, Ser. Khim., (1973) 951.
8 A.Z. Rubezhov, A.S. Ivanov and S.P. Gubin, Izv. Akad. Nauk SSSR, Ser. Khim., (1974) 1902.
9 A.S. Ivanov, A.Z. Rubezhov and S.P. Gubin, Izv. Akad. Nauk SSSR, Ser. Khim., (1974) 931.
10 A.Z. Rubezhov, A.S. Ivanov and S.P. Gubin, Izv. Akad. Nauk SSSR, Ser. Khim., (1974) 2651.
11 A.Z. Rubezhov, A.S. Ivanov and S.P. Gubin, Izv. Akad. Nauk SSSR, Ser. Khim., (1975) 1196.
12 A.Z. Rubezhov, A.S. Ivanov and S.P. Gubin, Izv. Akad. Nauk SSSR, Ser. Khim., (1976) 2348.
13 T.N. Salnikova, V.G. Andrianov, A.S. Ivanov, A.Z. Rubezhov and Yu.T. Struchkov, Koord. Khim., 3 (1977) 599.
14 A.Z. Rubezhov, A.S. Ivanov and S.P. Gubin, Izv. Akad. Nauk SSSR, Ser. Khim., in press.
15 J. Powell and B.L. Shaw, J. Chem. Soc. A, (1968) 583.
16 A.N. Nesmeyanov, R.B. Materikova and N.S. Kochetkova, Izv. Akad. Nauk SSSR, Ser. Khim., (1963) 1334.
17 W. Kitching, T.S. Sakakiyama, Z. Rappoport, P.D. Sleezer, S. Winstein and W.G. Young, J. Amer. Chem. Soc., 94 (1972) 2329.
18 A.S. Ivanov, Candidate's thesis, Moscow, INEOS, 1974, p. 72.
19 A.T.T. Hsich and M.J. Mays, Transition Metals, Part 2, London, 1972, 43.
20 R.F. Heck and C.P. Ross, J. Amer. Chem. Soc., 86 (1964) 2580.
21 R.A. Zelonka and M.C. Baird, J. Organometal. Chem., 44 (1972) 383.
22 A. Kross, Vvedenie v prakticheskuyu infrakrasnuyu spektroskopiyu (Introduction to Practical Infrared Spectroscopy), Moscow IL, 1961.
23 L.A. Fedorov, Usp. Khim., 39 (1970) 1389.
24 A.Z. Rubezhov, Candidate's thesis, Moscow, INEOS, 1967, p. 31.
25 H.P. Fritz, Advan. Organometal. Chem., 1 (1964) 40.
26 G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kroner, W. Oberkirch, K. Tanaka, E. Steinrucke, D. Walter and H. Zimmermann, Angew. Chem. Int. Ed., 5 (1966) 151.
27 V.I. Sokolov, V.V. Bashilov, L.M. Anishenko and O.A. Reutov, J. Organometal. Chem., 71 (1974) C4.
28 O.A. Reutov, I.P. Beletskaya and V.I. Sokolov, Mekhanizmy reaktsii metalloorganicheskikh soedinenii (Mechanisms of Reactions of Organometallic Compounds), Khimiya, Moscow, 1972.
29 W. Kitching, M.Z. Bullpitt, P.D. Huser and S. Winstein, J. Organometal. Chem., 34 (1972) 233.
30 T.A. Smolina, V.A. Kolevin and O.A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim., (1963) 2235.
31 S.P. Gubin, A.Z. Rubezhov and L.I. Voronchkhina, J. Organometal. Chem., 149 (1978) 123.