CARBENOID INSERTION OF ZERO-VALENT PLATINUM AND PALLADIUM INTO MERCURY SALTS OF METAL CARBONYLS

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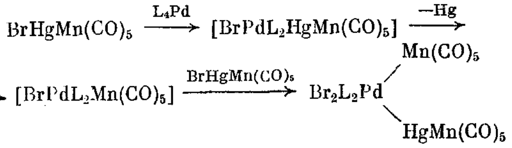
Previously it was shown that the ability of carbenoid particles $L_2M(0)$ to be inserted across the mercury–element bond has a general character for a number of elements (halogens, C, Si, Ge, Sn, etc.) [1] and, in particular, extends to the Hg derivative of an Fe carbonyl [2]. A source of carbenoids are the zero-valent Pt and Pd complexes with either PPh_3 or dibenzylideneacetone as the ligands. Insertion across the Hg–M bond has special interest as a method for building oligometallic chainlets that contain several different metals. We were the first to realize this principle on the example of chainlets composed of four metal atoms [2-4], which principle was then developed further [5].

We studied the behavior of the Hg salts of the Mn, Re, and Co carbonyls in the given reaction. Both the symmetrical derivatives and the halides were used. Using various combinations of the reactants we obtained end products of variable structure; in a number of cases the products could not be characterized: the elemental composition differed strongly from the expected structures, and the IR spectra had absorption bands that corresponded to bridge CO groups. A comparison with the literature data, relating to the reaction of L_2PtCl_2 with $NaMn(CO)_5$ [6], shows that the formation of cluster structures could be expected here.

The mercuribromides of the Mn and Re pentacarbonyls gave a different result when reacted with $Pt(PPh_3)_3$: demercuration proceeds much more easily in the case of Mn, whereas the trimetal derivative could be isolated in the case of Re.

$$BrHgMn(CO)_5 + L_3Pt \xrightarrow[-Hg]{} BrPtL_2Mn(CO)_5$$
$$BrHgRe(CO)_5 + L_3Pt \longrightarrow BrL_2PtHgRe(CO)_5$$

In the case of the same Mn derivative a product, containing Hg, was obtained for the more nucleophilic $Pd(PPh_3)_4$, which, based on the elemental analysis, corresponded to a double oxidative addition with the formation of the Pd(IV) derivative.



$$BrHgMn(CO)_5 \xrightarrow{L_4Pd} [BrPdL_2HgMn(CO)_5] \xrightarrow{-Hg} [BrPdL_2Mn(CO)_5] \xrightarrow{BrHgMn(CO)_5} Br_2L_2Pd(Mn(CO)_5)(HgMn(CO)_5)$$

Although Pd(IV) derivatives are quite rare, it is known that their formation is facilitated by the presence of electron-acceptor groups, for example C_6F_5 [7]. The presence of two $Mn(CO)_5$ groups, which have an analogous electronic effect, can stabilize the postulated structure.

The reaction with symmetrical $Hg[M(CO)_n]_2$ compounds goes much slower and is complicated by side processes, of which the main one is exchange of the carbonyl ligand by the PPh_3 present in solution. This is responsible for the deviation in the analytical data from those calculated for the product of inserting L_2Pt into $Hg[Mn(CO)_5]_2$. In the case of the Hg salt of the Co carbonyl the exchange of CO by 2 equiv. of PPh_3 proceeds with exceeding ease and the quite insoluble $Hg[Co(CO)_3PPh_3]_2$ is removed from the reaction sphere as a precipitate; it was identified by comparing with an authentic specimen. For Pd the desired insertion product could be obtained by using a mixture of $Pd_2(dba)_3$ and an equivalent amount of 1,2-bis(diphenylphosphino)ethane (Diphos, PP)

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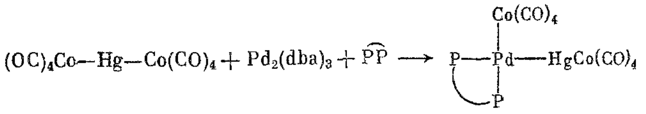

$$(OC)_4Co{-}Hg{-}Co(CO)_4 + Pd_2(dba)_3 + \overset{\frown}{PP} \longrightarrow \overset{Co(CO)_4}{\underset{P}{P{-}Pd}}{-}HgCo(CO)_4$$

EXPERIMENTAL

All of the reactions were run in an argon atmosphere, in dry solvents. The IR spectra were recorded on a UR-10 instrument. The melting points were determined in sealed capillaries.

Bis(triphenylphosphine)pentacarbonylmanganeseplatinum Bromide (I). A solution of 0.650 g of $Pt(PPh_3)_3$ in 20 ml of C_6H_6 was added to a suspension of 0.320 g of $BrHgMn(CO)_5$ in 30 ml of C_6H_6, after which 5 ml of THF was added, and the mixture was stirred for 8 h, and then for another 1.5 h at 40°C. The deposited Hg was filtered, the filtrate was evaporated to 20 ml, and the residue was treated with 8 ml of hexane and cooled to give 0.46 g (60%) of light brown (I), decompn. point 158°. Found: C 48.58; H 3.28%. $C_{41}H_{30}BrP_2MnPtO_5$. Calculated: C 49.49; H 3.02%. Infrared spectrum (KBr, cm^{-1}): ν(CO) 1835 s, 1890 w, 1950 m; ν (C_{ar}H): 3065 m; δ (C_{ar}–H): 695 s, 750 s; ν (C_{ar}–C_{ar}): 1440 s, 1485 m.

Pentacarbonylrheniummercuri-bis(triphenylphosphine)platinum Bromide (II). To a suspension of 0.450 g of $BrHgRe(CO)_5$ in 70 ml of C_6H_6 was added a solution of 0.750 g of $Pt(PPh_3)_3$ in 25 ml of C_6H_6. All of the salt dissolved in 15 min. The red solution was filtered from the grayish green precipitate, 25 ml of hexane was added and the whole was let stand in the refrigerator. The orange precipitate of (II) was filtered, washed in succession with chilled benzene and hexane, and dried in vacuo. The yield was 0.47 g (45%), decompn. point 114-117°. Found: C 40.00; H 2.96; Hg 14.93%. $C_{41}H_{30}BrP_2HgRePtO_5 \cdot C_6H_6$. Calculated: C 40.17; H 2.56; Hg 14.39%. Infrared spectrum (KBr, cm^{-1}): ν(CO) – 1685 m, 1890 s, 1910 s, 1955 s; ν (C_{ar}–H): 3065 m; δ (C_{ar}–H): 700 s, 725 s, 750 s.

(Pentacarbonylmanganesemercuri)-(pentacarbonylmanganese) bis(triphenylphosphine)palladium Dibromide (III). To a suspension of 0.4 g of $BrHgMn(CO)_5$ in 40 ml of C_6H_6 was added a solution of 1.05 g of $Pd(PPh_3)_4$ in 30 ml of C_6H_6. The mixture was stirred for 48 h, and the obtained green precipitate of (III) was separated, washed in succession with hot benzene and pentane, and dried in a vacuum-desiccator. The yield was 0.45 g (77%), decompn. point 189° (from acetone). Found: C 41.36; H 2.55; Br 10.87; Hg 14.56%. $C_{49}H_{36}Br_2P_2O_{11}HgMn_2Pd$. Calculated: C 40.81; H 2.51; Br 11.10; Hg 13.93%. Infrared spectrum (KBr, cm^{-1}); ν (CO): 1710 m (acetone), 1965 s, 1975 s, 1985 s, 2010 s, 2060 s.

Bis(triphenylphosphine)bis(pentacarbonylmanganese)platinum (IV). To a suspension of 0.3 g of $Hg[Mn(CO)_5]_2$ in 20 ml of THF was added a solution of 0.65 g of $Pt(PPh_3)_3$ in 40 ml of C_6H_6 and the mixture was stirred for 48 h. The obtained brown precipitate contained Hg. In order to completely precipitate the Hg the stirred mixture was heated in the sunlight at 40°, filtred from the Hg, passed through a thin layer of silica gel, and evaporated to 1/3 volume. After adding 20 ml of hexane the solution was cooled to give 0.27 g (47%) of brown (IV), decompn. point 130-135°. Found: C 50.64; H 3.79; P 6.26%. $C_{46}H_{30}P_2O_{10}Mn_2Pt$. Calculated: C 49.77; H 2.71; P 5.59%.

(Tetracarbonylcobaltmercuri)-(tetracarbonylcobalt)-1,2-bis-(diphenylphosphinoethane)palladium (V). To a suspension of 0.5 g of $Pd_2(dba)_3 \cdot C_6H_6$ in 25 ml of C_6H_6 was added 0.4 g of 1,2-bis(diphenylphosphino)ethane. The mixture was stirred until the complex dissolved. To the solution was added 0.54 g of $Hg[Co(CO)_4]_2$ in 20 ml of C_6H_6. After 10 min the brown precipitate was filtered, washed in succession with hot benzene and hexane, and dried in vacuo to give 0.57 g (52%) of (V), decompn. point 164°. Found: C 42.66; H 3.04; Hg 17.61%. $C_{34}H_{24}P_2O_8Co_2HgPd \cdot C_6H_6$. Calculated: C 42.66; H 2.66; Hg 17.86%. Infrared spectrum (KBr, cm^{-1}): ν(CO) – 1865 s, 1885 s, 1960 s, 2030 m; ν (C_{ar}–H): 3060 m, ν(C_{al}–H): 2920 w, 2960 w; ν(C_{ar}–C_{ar}): 1440 s; δ (C_{ar}–H): 695 s, 715 s, 750 s.

CONCLUSIONS

1. Zero-valent Pt and Pd complexes insert themselves into the Hg salts of Mn, Re, and Co carbonyls to give compounds that contain chainlets composed of different metals of type Re–Hg–Pt, Mn–Hg–Pd–Mn, Co–Hg–Pd–Co.

2. The double oxidative addition of $Pd(PPh_3)_4$ to $BrHgMn(CO)_5$ gave the Pd(IV) derivative, which was stabilized by two electron-acceptor metal carbonyl groupings.

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