

Journal of Organometallic Chemistry, 389 (1990) C23–C25
 Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
 JOM 20931PC

Preliminary communication

Synthesis of organomercury–platinum complexes by reaction of platinum hydrides with organomercurials

Andreas Handler, Paul Peringer ^{*}

*Institut für Anorganische und Analytische Chemie der Universität Innsbruck, Innrain 52a,
 A-6020 Innsbruck (Austria)*

and Ernst P. Müller

*Institut für Organische und Pharmazeutische Chemie der Universität Innsbruck, Innrain 52a,
 A-6020 Innsbruck (Austria)*

(Received February 23rd, 1990)

Abstract

$[\text{Pt}(\text{pp}_3\text{-P,P',P'',P'''}\text{)H}]\text{O}_3\text{SCF}_3$ and $[\text{Pt}(\text{np}_3\text{-N,P,P',P''})\text{H}]\text{O}_3\text{SCF}_3$ ($\text{pp}_3 = \text{P}[\text{CH}_2\text{CH}_2\text{PPh}_2]_3$, $\text{np}_3 = \text{N}[\text{CH}_2\text{CH}_2\text{PPh}_2]_3$) have been shown to react with phenylmercury hydroxide to give $[\text{PhHgPt}(\text{pp}_3\text{-P,P',P'',P'''}\text{)O}_3\text{SCF}_3$ and $[\text{PhHg}(\text{np}_3\text{-N,P,P',P''})\text{O}_3\text{SCF}_3$, which have been characterized by ^{31}P , ^{195}Pt and ^{199}Hg NMR spectroscopy.

Organomercury–platinum complexes involving a R–Hg–Pt linkage are stable when R is a strongly electronegative group (e.g. CF_3 or C_6F_5) [1,2] or when there is steric crowding near the platinum–mercury bond. Otherwise, extrusion of elemental mercury gives organoplatinum compounds [1]. The steric crowding mentioned above may originate either from the organic group attached to mercury (e.g. aryl groups with methyl [2] or chlorine [3–5] substituents in the 2- and 5-positions) or from the ligands coordinated to platinum. In the case of $[\text{MeHgPt}(\text{np}_3\text{-N,P,P',P''})]\text{BPh}_4$ ($\text{np}_3 = \text{N}[\text{CH}_2\text{CH}_2\text{PPh}_2]_3$), it was the steric effect of the phenyl groups of the np_3 ligand which was thought to stabilize the Me–Hg–Pt linkage [6].

All organomercury–platinum complexes have previously been prepared by the reaction of R_2Hg [1–4] or RHgX ($\text{X} = \text{halogen}$) [5,7,8] with 14-electron or 16-electron zero-valent platinum intermediates. Most of the reactions involved $[\text{Pt}(\text{PPh}_3)_2]$ generated either from $[\text{Pt}(\text{PPh}_3)_3]$ [1,2,7,8], or from $[\text{Pt}(\text{PPh}_3)\text{C}_2\text{H}_4]$ [3–5], but one reaction involved $[\text{Pt}(\text{np}_3\text{-P,P',P''})]$ generated from $[\text{Pt}(\text{np}_3\text{-P,P',P''})(\text{PPh}_3)]$ [6].

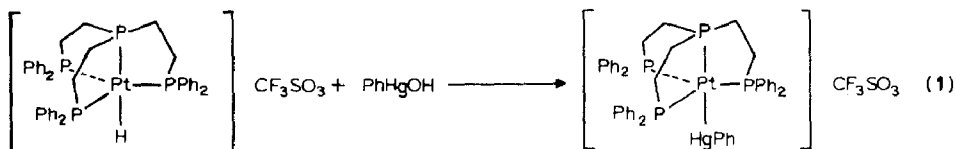
We describe the preparation of organomercury–platinum complexes by the reaction of platinum hydrides with organomercury compounds. This method has been used for the synthesis of $[\text{RHgPt}(\text{pp}_3\text{-P,P',P'',P'''}\text{)O}_3\text{SCF}_3$ ($\text{pp}_3 = \text{P}[\text{CH}_2\text{CH}_2\text{PPh}_2]_3$), for which no zero-valent platinum precursor is available.

Table 1
NMR data ^a

	1	2
$\delta(\text{P}_A)$	36.3 d	26.3
$\delta(\text{P}_B)$	155.9 q	
$\delta(^{195}\text{Pt})$	-5598 dq	-4155 q
$\delta(^{199}\text{Hg})$	2066 dq	1479 q
$J(\text{P}_A-\text{P}_B)$	7	
$^1J(\text{Pt}-\text{P}_A)$	2891	3135
$^1J(\text{Pt}-\text{P}_B)$	1793	
$^2J(\text{Hg}-\text{P}_A)$	187	161
$^2J(\text{Hg}-\text{P}_B)$	1460	
$^1J(\text{Hg}-\text{Pt})$	4322	5483

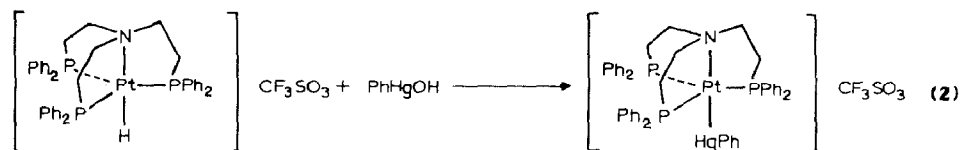
^a Notation: $\text{P}_B[\text{CH}_2\text{CH}_2\text{P}_A\text{Ph}_2]_3$, $\text{N}[\text{CH}_2\text{CH}_2\text{P}_A\text{Ph}_2]_3$; d = doublet, q = quartet; chemical shifts in ppm relative to 85% H_3PO_4 , aqueous 1 M Na_2PtCl_6 and aqueous $\text{Hg}(\text{ClO}_4)_2$ (1 mmol HgO/mL 60% HClO_4); coupling constants in Hz; solvent $\text{CH}_2\text{Cl}_2/\text{MeOH}$ 2/1; $T = 223$ K.

The reaction between $[\text{Pt}(\text{pp}_3\text{-P}, \text{P}', \text{P}'', \text{P}''')\text{H}]\text{O}_3\text{SCF}_3$ [9] and phenylmercury hydroxide in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ at ambient temperature gave $[\text{PhHgPt}(\text{pp}_3\text{-P}, \text{P}', \text{P}'', \text{P}''')]\text{O}_3\text{SCF}_3$ (1), as shown in eq. 1:



Product 1 was characterized by ^{31}P , ^{195}Pt , and ^{199}Hg NMR spectroscopy. The ^{31}P NMR spectrum shows an AM_3 spin pattern consisting of a quartet and a doublet attributable respectively to the central and the terminal phosphorus atoms of the pp_3 ligand. Both signals have satellites due to one-bond $\text{Pt}-\text{P}$ and two-bond $\text{Hg}-\text{P}$ couplings. The $\text{Hg}-\text{P}$ *cis*- and *trans*-couplings differ by an order of magnitude as previously observed [3–5]. The ^{31}P chemical shift for the central phosphorus atom of the pp_3 ligand and the ^{195}Pt shift are remarkably large. The NMR data are listed in Table 1.

$[\text{Pt}(\text{np}_3\text{-N}, \text{P}, \text{P}', \text{P}'')\text{H}]\text{O}_3\text{SCF}_3$ [10] reacts analogously with organomercurials, as illustrated in eq. 2:



The NMR data for 2 are included in Table 1, and are similar to those for $[\text{MeHgPt}(\text{np}_3\text{-N}, \text{P}, \text{P}', \text{P}'')]\text{BPh}_4$, which was prepared from $[\text{Pt}(\text{np}_3\text{-P}, \text{P}', \text{P}'')]\text{PPh}_3$ and MeHgCl [6]. A comparison of the NMR data for 1 and 2 reveals marked differences in the ^{195}Pt and ^{199}Hg shifts. The $\text{Hg}-\text{Pt}$ coupling in 1 is smaller than that in 2 in keeping with the relative *trans* influences of N- and P-donor ligands.

Preliminary experiments indicate that platinum hydrides react with other mercury complexes and also with compounds of other metals to give heterobimetallic systems.

References

- 1 V.I. Sokolov, V.V. Bashilov and O.A. Reutov, *J. Organomet. Chem.*, 97 (1975) 299.
- 2 V.I. Sokolov, V.V. Bashilov and O.A. Reutov, *J. Organomet. Chem.*, 111 (1976) C13.
- 3 O. Rossell, J. Sales and M. Seco, *J. Organomet. Chem.*, 236 (1983) 415.
- 4 M. Crespo, O. Rossell, J. Sales and M. Seco, *J. Organomet. Chem.*, 273 (1984) 415.
- 5 J. Calvet, O. Rossell and M. Seco, *Transition Met. Chem.*, 9 (1984) 208.
- 6 C.A. Ghilardi, S. Midollini, S. Moneti, A. Orlandini, G. Scapacci and D. Dakternieks, *J. Chem. Soc., Chem. Commun.*, (1989) 1686.
- 7 O.A. Reutov, V.I. Sokolov, G.Z. Suleimanov and V.V. Bashilov, *J. Organomet. Chem.*, 160 (1978) 7.
- 8 G.Z. Suleimanov, V.V. Bashilov, A.A. Musaev, V.I. Sokolov and O.A. Reutov, *J. Organomet. Chem.*, 202 (1980) C61.
- 9 $[\text{Pt}(\text{pp}_3\text{-P,P',P'',P'''})\text{H}]\text{BPh}_4$ has been previously reported: P. Brüggeller, *Inorg. Chim. Acta*, 129 (1987) L27.
- 10 $[\text{Pt}(\text{np}_3\text{-N,P,P',P''})\text{H}]\text{BPh}_4$ has been previously mentioned: S. Midollini et al., to be published as quoted in C.A. Ghilardi, S. Midollini, S. Moneti, A. Orlandini and J.A. Ramirez, *J. Chem. Soc., Chem. Commun.*, (1989) 304.