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[$Hg(EPPh_2CHPPh_2)_2$] (E = S, Se, Te): Organomercury Compounds Without Mercury–Carbon Bonds

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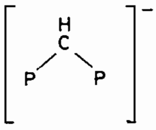
Abstract

The first transition metal complexes of deprotonated [(diphenylphosphino)methyl] diphenylphosphine chalcogenides are reported. ($EPPh_2CHPPh_2$)Li, E = Se, Te, was obtained from $(PPh_2)_2CHLi$ and elemental E. The title compounds are formed from ($EPPh_2CHPPh_2$)Li and $HgCl_2$. The ligands act as P, E-bonded chelates. The new compounds were characterized by ^{31}P and ^{199}Hg NMR spectroscopy.

Introduction

Deprotonated $CH_2(PPh_2)_2$ (**1**)** has been shown to bind either through the methine carbon and one phosphorus atom or through two phosphorus atoms when acting as the bidentate ligand [1–5]. Deprotonated $CH_2[P(S)Ph_2]_2$ (**2**) has been reported to act as a C, S bonded chelate [6]. Deprotonated $CH[P(S)PPh_2]_3$ (**3**) coordinates as tridentate sulfur ligand in different metal complexes including mercury [7–10]. Deprotonated $EPPh_2CH_2PPh_2$ (**4**) represents thus an ambidentate ligand system with C, P and E as potential donor sites. No metal complexes apart from ($EPPh_2CHPPh_2$)Li (**4**, E = S) [4] have been reported. This compound contains lithium attached to phosphorus according to ^{31}P and ^{7}Li NMR measurements [4]. We report here on mercury compounds of [$EPPh_2CHPPh_2$] , with E = S, Se and Te.



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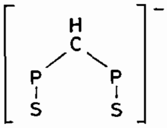

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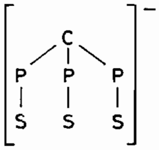

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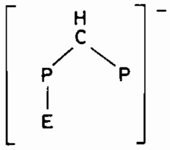

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Results and Discussion

($SPPh_2CHPPh_2$)Li is formed from $SPPh_2CH_2PPh_2$ and BuLi in THF [4]. The selenium analogue (**4**, E = Se) is formed in a corresponding reaction, however selenium transfer from phosphorus to BuLi occurs in a side reaction leading to $CH_2(PPh_2)_2$, $(PPh_2)_2CHLi$ and $BuSe_nLi$. ($SePPh_2CHPPh_2$)Li is however obtained in a clean reaction from (PPh_2)CHLi and elemental selenium. The formation of a P–Se bond instead of a C–Se bond in this reaction is not unexpected since $(PPh_2)_2CHLi$ contains lithium bound to the phosphorus atoms but not to the carbon atom [4, 5]. Selenium thus inserts into a P–Li bond.

Tellurium does not react with $CH_2(PPh_2)_2$ to yield $TePPh_2CH_2PPh_2$. ($TePPh_2CHPPh_2$)Li (**4**, E = Te) is however formed from $(PPh_2)_2CHLi$ and elemental tellurium.

The NMR parameters of the compounds ($EPPh_2CHPPh_2$)Li, E = S, Se and Te are listed in Table I.

TABLE I. NMR Parameters of ($EPPh_2CHPPh_2$)Li[a]

E	$\delta(P)$[b]	$\delta(P_E)$	$^2J(P,P)$	T (K)
S[c]	−19.7	42.2	166	300
Se	−15.3	33.3[d]	168	193
Te	−14.2	−19.2[e]	164	213

[a] In ppm to high frequency of 85% H_3PO_4, coupling constants in Hz, solvent: THF, instrument: Bruker WP-80. [b] $\delta(P)$ of $CH_2(PPh_2)_2$: −22.6. [c] Similar data have been reported [4] (solvent Et_2O). [d] $^1J(^{77}Se, ^{31}P)$: 610. [e] $^1J(^{125}Te, ^{31}P)$: 1476.

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**In all sketches of structures only the connectivity is shown. There is no attempt to define bond orders. The formulae are drawn without the phenyl substituents.

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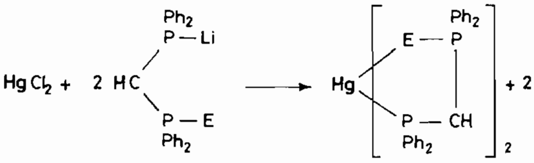
TABLE II. NMR Parameters of $[Hg(EPPh_2CHPPh_2)_2]^a$

E	δ(P)	$\delta(P_E)$	^1J(Hg,P)	J(PCP)	J(PHgP)	δ(Hg)	^3J(Hg,P)
S	19.2	48.1	4456	98	144	2332	65
Se	22.7	38.1	3963	118	115	2351	38
Te	31.5	2.1	2963	147	68	b	c

[a] In ppm to high frequency of 85% H_3PO_4 or aqueous $Hg(ClO_4)_2$ (2 mmol HgO/ml 60% H_3PO_4), coupling constants in Hz, solvent: THF, 213 K, instrument: Bruker WP-80. [b] Insufficient solubility prevented the collection of ^{199}Hg NMR data. [c] Not resolved.

The chemical shift of the P(E) phosphorus atom decreases in the row E = S → Te as expected [11]. The resonance position of the other phosphorus atom is shifted to a high frequency when going from S to Te. The tellurium phosphorus bond in $(TePPh_2CHPPh_2)Li$ is kinetically remarkably stable; the AB ^{31}P NMR pattern of the compound appears only slightly broadened at ambient temperature.

The reaction of 2 equivalents of $(EPPh_2CHPPh_2)Li$, prepared *in situ,* with $HgCl_2$ in THF at −60 °C, gave the title compounds $[Hg(EPPh_2CHPPh_2)_2]$ (eqn. (1))



(1)

The NMR data of the compounds are summarized in Table II. The ligands are thought to coordinate via the phosphorus and the E atoms for the following reasons: the magnitude of the mercury–phosphorus coupling constants clearly demonstrates the presence of one bond couplings. This excludes the existence of a (methine) carbon–mercury bond since diorganomercury compounds are weak electron acceptors unless the organic groups are electronwithdrawing groups. The coordination of E to mercury is inferred from the position of the ^{199}Hg resonance. Compounds of the type $[Hg(PR_3)_2]^{2+}$ have chemical shifts in the region of 1200 ppm. The coordination of additional ligands is typically accompanied by a high frequency shift of the mercury-199 resonance [11]. The values of ^1J(Hg,P) and ^2J(PHgP) are very sensitive to E. The variation indicates that the Hg–E interactions progressively weaken and the P–Hg–P bonding angles become more open in the sequence E = Te → S [12, 13]. The decrease in ^1J(HgP) for E = S → Te closely resembles that for the compounds $HgX_2(PR_3)_2$, X = Cl, Br, I [14, 15]. In both series the difference in ^1J(Hg,P) between the compounds involving the two heavier elements (Te–Se or I–Br) is about twice the difference between the compounds involving the two lighter elements (Se–S or Br–Cl). Decomposition occurs as solutions of $Hg(EPPh_2CHPPh_2)_2$ are allowed to warm.

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