Notizen

Complexes with Carbon Sulfides and Selenides as Ligands, XXIII[1)]

Synthesis of $Pt(CS)(PPh_3)_2$ and $Pt(CE)(dpmb)$ (E = S, Se): The First Mononuclear Thio- and Selenocarbonyl Complexes of Platinum(0)

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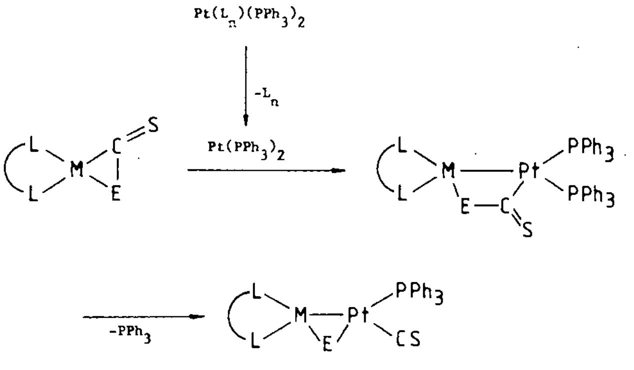
$(PPh_3)_2Pt(\mu-CS_2)Pt(PPh_3)_2$ (1) and $(dpmb)Pt(\mu-CE_2)Pt(PPh_3)_2$ (2: E = S; 3: E = Se) on heating at 40–70°C give the complexes $Pt(CS)(PPh_3)_2$ (4) and $Pt(CE)(dpmb)$ (5: E = S; 6 E = Se), which are the first mononuclear thio- and selenocarbonyl complexes of platinum(0).

The most common method of generating a CS or CSe ligand in the coordination sphere of a transition metal, namely the abstraction of a sulfur or selenium atom from coordinated CS_2 or CSe_2 by phosphanes[2,3)], has failed thus far with Pd(0) and Pt(0). Treatment of the complexes $M(\eta^2-CS_2)(PPh_3)_2$ and $M(\eta^2-CSe_2)(PPh_3)_2$ (M = Pd, Pt) with PMe_3, PMe_2Ph, $PMePh_2$ etc. does not lead to the formation of the corresponding thio- and selenocarbonyl compounds $M(CE)(PPh_3)_2$ (E = S, Se), but to mono- or dinuclear products containing $PR_3^+CS_2^-$, CS_3^{2-}, or $C_2Se_4^{2-}$ units as ligands[4,5)]. Recently, we[1,6)] as well as Walker, Farrar et al.[7,8)] observed, however, that the chelate compounds $Pd(\eta^2-CSSe)(dppe)$*), $Pt(\eta^2-CS_2)(dppe)$, $Pt(\eta^2-CSSe)(dppe)$, and $Pt(\eta^2-CSSe)(dpmb)$ react with $Pt(C_2H_4)(PPh_3)_2$ or $Pt(PPh_3)_4$ to give dinuclear thiocarbonyl complexes $[L_2M(\mu-E)Pt(CS)(PPh_3)]$ (L_2 = dppe or dpmb). As we assumed that compounds of general composition $[L_2M(\mu-CSE)Pt(PPh_3)_2]$ are intermediates in the formation of $[L_2M(\mu-E)Pt(CS)(PPh_3)]$ (see Scheme 1)[1)], we tried to find out whether thermolysis of stable species such as $[(PPh_3)_2Pt(\mu-CS_2)Pt(PPh_3)_2]$ (1), $[(dpmb)Pt(\mu-CE_2)Pt(PPh_3)_2]$ (2, 3), $[(dpmb)Pd(\mu-CE_2)Pt(PPh_3)_2]$ (E = S, Se)[1,6)] would give dinuclear homo- and hetero-metallic complexes of a similar type. It should be mentioned that cocondensation of CS produced by microwave discharge through CS_2 vapour with nickel atoms in an argon matrix at 10 K forms $Ni(CS)_4$[9)], but that *mononuclear* thio- and selenocarbonyl complexes of *palladium(0)* and *platinum(0)* are, to the best of our knowledge, still unknown.

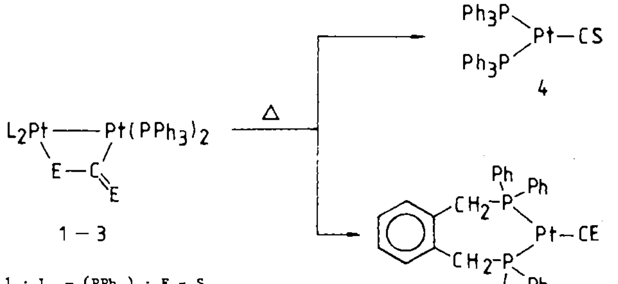
Scheme 1. [L⌒L = dppe or dpmb; L_n = C_2H_4 or $(PPh_3)_2$; E = S, Se; M = Pd, Pt]



Results

Heating suspensions of the nearly insoluble compounds 1–3 in dichloromethane or benzene to 40–70°C results in the formation of orange solutions, from which microcrystalline solids 4–6 are isolated. Although the IR spectra show an intense band at 1305 cm^{-1} (for 4, 5) and at 1110 cm^{-1} (for 6) which corresponds to the presence of a terminal CS or CSe ligand and would thus be in agreement with a complex of general type $[L_2Pt(\mu-E)Pt(CE)(PPh_3)]$ (E = S, Se), the elemental analyses indicate that mononuclear products are obtained.

Scheme 2



1 : L_2 = $(PPh_3)_2$; E = S
2 : L_2 = dpmb; E = S
3 : L_2 = dpmb; E = Se

5 : E = S ; 6 : E = Se

In accord with the trigonal coordination at the platinum atom (see Scheme 2), the ^{31}P-NMR spectra of 4–6 show only a singlet line for the two equivalent phosphorus atoms which is accompanied by ^{195}Pt satellites. In the ^1H-NMR spectra of 5 and 6 the observation of one signal (as a virtual triplet) for the CH_2 protons of the dpmb ligand further supports the proposed structure.

Analogues of 1–3, the compounds $[(PPh_3)_2Pt(\mu-CSe_2)Pt(PPh_3)_2]$ and $[(dpmb)Pd(\mu-CSe_2)Pt(PPh_3)_2]$[1)], also form red solutions if heated in dichloromethane. Although the solid residues obtained after evaporation of the solvent showed an absorption in the region of 1110 cm^{-1}, all attempts to isolate a pure product failed. We assume that in the presence of metal-containing species there is a general tendency for thio- and selenocarbonyl palladium(0) and

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*) Abbreviations used: dppe = 1,2-$C_2H_4(PPh_2)_2$; dpmb = 1,2-$C_6H_4(CH_2PPh_2)_2$.

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platinum(0) complexes of the type $M(CE)L_2$ (M = Pd, Pt) to undergo subsequent reactions which may lead either to clusters or polymeric species with bridging CE ligands. Examples for E = O, e.g., $Pt_3(CO)_3(PR_3)_n$[10], $Pd_3(CO)_3(PPh_3)_n$[11] (*n* = 3 or 4), $Pd_7(CO)_7(PMe_3)_7$[12], and $Pd_{23}(CO)_{22}(PEt_3)_{10}$[13], with phosphanes as co-ligands are already known.

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Experimental

All operations were carried out under purified nitrogen. The starting materials **1**–**3** were prepared by a published procedure[1].

(Thiocarbonyl)bis(triphenylphosphane)platinum(0) (**4**): A suspension of 788 mg (0.52 mmol) of **1** in 10 ml of benzene was heated to 60–70°C and stirred at this temperature until a clear red-brown solution was formed. After cooling to room temperature the solution was concentrated to ca. 5 ml in vacuo and chromatographed on Al_2O_3 (Woelm, neutral, activity grade IV) with benzene as solvens. The orange fraction was evaporated in vacuo, and the residue was repeatedly washed with hexane. An orange microcrystalline powder was obtained. Yield 266 mg (67%), m.p. 112°C (dec.). – IR (Nujol): ν(CS) 1305 cm^{-1}. – ^{1}H NMR (CH_2Cl_2): δ = 7.26 (m) [C_6H_5]. – ^{31}P NMR [C_6D_6; 1% Cr(acac)$_3$]: δ = 24.34 (s), *J*(PtP) = 2440 Hz.

$C_{37}H_{30}P_2PtS$ (763.7) Calcd. C 58.18 H 3.95 Pt 25.54
Found C 58.33 H 4.35 Pt 24.87

[1,2-Bis(diphenylphosphinomethyl)benzene](thiocarbonyl)platinum(0) (**5**): Analogously as described for **4**, heating a suspension of 200 mg (0.14 mmol) of **2** in 5 ml of dichloromethane to 40°C led to an orange microcrystalline powder, yield 86 mg (42%), m.p. 96°C (dec.). – IR (Nujol): ν(CS) 1305 cm^{-1}. – ^{1}H NMR (CH_2Cl_2): δ = 7.16 (m) [C_6H_4]; 1.05 (vt), *N* = 6 Hz, *J*(PtH) = 48 Hz [CH_2]. – ^{31}P NMR [C_6D_6; 1% Cr(acac)$_3$]: δ = 20.49 (s), *J*(PtP) = 2900 Hz.

$C_{33}H_{28}P_2PtS$ (713.6) Calcd. C 55.53 H 3.95 Pt 27.33
Found C 55.44 H 4.26 Pt 27.10

[1,2-Bis(diphenylphosphinomethyl)benzene](selenocarbonyl)platinum(0) (**6**): A suspension of 300 mg (0.19 mmol) of **3** in 10 ml of benzene was heated to 60–70°C and stirred at this temperature until a clear red-brown solution was formed. After cooling to room temperature, a dark red oil precipitated which was separated from the mother liquor, washed with ether, and stirred in ether suspension until a solid residue was obtained. It was filtered off, repeatedly washed with ether, and recrystallized from CH_2Cl_2/OEt_2 to give orange-red crystals. Yield 95 mg (65%), m.p. 128°C (dec.). – IR (Nujol): ν(CSe) 1110 cm^{-1}. – ^{1}H NMR (CH_2Cl_2): δ = 7.24 (m) [C_6H_4]; 1.13 (vt), *N* = 6 Hz, *J*(PtP) = 44 Hz [CH_2]. – ^{31}P NMR [CH_2Cl_2/C_6D_6 10:1; 1% Cr(acac)$_3$]: δ = 9.02 (s), *J*(PtP) = 2880 Hz.

$C_{33}H_{28}P_2PtSe$ (760.6) Calcd. C 52.10 H 3.71 Pt 25.14
Found C 52.32 H 4.16 Pt 25.60

CAS Registry Numbers

1: 102086-58-8 / **2**: 114032-40-5 / **3**: 114057-07-7 / **4**: 114032-41-6 / **5**: 114032-42-7 / **6**: 114032-43-8

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