Organometallics 1983, *2*, 891–895

Reactions of (Phosphine)palladium(0) Complexes with Thiocarbonyl Selenide and the X-ray Crystal Structure of $[1,2\text{-C}_6\text{H}_4(\text{CH}_2\text{PPh}_2)_2]\text{Pd}(\eta^2\text{-CSSe})$[1]

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Received January 26, 1983

The reactions of $\text{Pd}(\text{P-}i\text{-Pr}_3)_n$ (n = 2 or 3) and $\text{Pd}(\text{PPh}_3)_4$ with CSSe yield the compounds $(\text{PR}_3)_2\text{Pd}(\eta^2\text{-CSSe})$ (**1**, **2**) for which a η^2-bonding mode via C and Se is indicated by infrared data. $(\text{PPh}_3)_2\text{Pd}(\eta^2\text{-CSSe})$ (**2**) reacts with the diphosphines $1,2\text{-C}_2\text{H}_4(\text{PPh}_2)_2$ (diphos) and $1,2\text{-C}_6\text{H}_4(\text{CH}_2\text{PPh}_2)_2$ (dpmb) by displacement of the PPh_3 ligands to form the chelate complexes $(\text{diphos})\text{Pd}(\eta^2\text{-CSSe})$ (**3**) and $(\text{dpmb})\text{Pd}(\eta^2\text{-CSSe})$ (**4**). From **2** and $1,2\text{-C}_6\text{H}_4(\text{Ph}_2)_2$ (dppb), the compound $\text{Pd}(\text{dppb})_2$ (**5**) is obtained. The molecular structure of **4** has been determined by X-ray investigation. **4** crystallizes in the space group $P2_1/c$ with a = 958.5 (13) pm, b = 1502 (2) pm, c = 2150 (5) pm, and β = 103.1 (2)°. The four atoms linked to palladium are approximately in one plane. The thiocarbonyl selenide unit is coordinated via C and Se with a S–C–Se angle of 141 (1)°. The C–Se and C–S distances are 180 (2) and 162 (2) pm; i.e., they are longer than in free CSSe. The Pd–P bond lengths (228.3 (5) pm trans to Se and 236.6 (5) pm trans to C) differ significantly reflecting the characteristic trans-lengthening effect of the CSSe carbon atom.

Introduction

The main reason for the present interest in the coordination chemistry of CS_2 and similar heteroallenes certainly is that CS_2 is a homologue of CO_2 and, therefore, metal complexes formed from CS_2 or heteroallenes can be regarded as model compounds for CO_2 activation. The fact is, however, that although today hundreds of transition-metal CS_2 complexes have been prepared,[2] little is known about analogous compounds containing CO_2 as a ligand.[3,4] It is thus not surprising that recently part of the activities in this area have concentrated on the reactivity of unsymmetrical molecules such as COS,[4,5] OCNR,[6] COSe,[7] and CSSe,[8,9] hoping that this could help to understand some of the difficulties encountered with the coordination of CO_2 itself.

We have been investigating the behavior of heteroallenes toward transition-metal bases of the general type $\text{C}_5\text{R}_5\text{ML}_2$ and $\text{C}_5\text{R}_5\text{MLL}'$ (R = H, Me; M = Co, Rh; L and L′ = PR_3, P(OR)_3, CO, C_2H_4, etc.)[2c,10] and have found that, e.g., the cobalt complexes $\text{C}_5\text{H}_5\text{Co}(\text{PMe}_3)_2$ and $\text{C}_5\text{H}_5\text{Co}(\text{PMe}_3)\text{CO}$ readily react with CS_2 to form $\text{C}_5\text{H}_5\text{Co}(\text{PMe}_3)(\eta^2\text{-CS}_2)$.[11] The reaction of $\text{C}_5\text{H}_5\text{Co}(\text{PMe}_3)_2$ with CSSe gives a mixture of $\text{C}_5\text{H}_5\text{Co}(\text{PMe}_3)(\eta^2\text{-CSSe})$ and $\text{C}_5\text{H}_5\text{Co}(\text{PMe}_3)\text{CS}$ from which the heteroallene complex can be easily separated.[8,12] We have been unable, as yet, to obtain suitable single crystals of $\text{C}_5\text{H}_5\text{Co}(\text{PMe}_3)(\eta^2\text{-CSSe})$, and thus we could only deduce from the reactivity of the compound (which on treatment with PPh_3 yields *quantitatively* $\text{C}_5\text{H}_5\text{Co}(\text{PMe}_3)\text{CS}$ and SePPh_3 but not $\text{C}_5\text{H}_5\text{Co}(\text{PMe}_3)\text{CSe}$ and SPPh_3)[8,12] that the thiocarbonyl selenide ligand is linked via C and Se to the cobalt atom. The possibility that CSSe can also coordinate via C and S has been demonstrated quite recently by the elegant work of Roper et al.,[9] who isolated both isomers (C, Se and C, S bonded) of the osmium complex $\text{Os}(\eta^2\text{-CSSe})(\text{CO})(\text{CN-}p\text{-tol})(\text{PPh}_3)_2$.

Since we also had previously studied the reactivity of (phosphine)palladium compounds toward CS_2,[13] COS,[14] and SCNR[15] in some detail, we became interested in investigating the reactivity of $\text{Pd}(\text{PR}_3)_n$ toward CSSe. Besides the synthesis of $(\text{PR}_3)_2\text{Pd}(\eta^2\text{-CSSe})$, the main goal of our research was to establish the coordination mode of thiocarbonyl selenide in this type of product and to see whether such species could be used (like the cobalt and rhodium compounds $\text{C}_5\text{H}_5\text{Co}(\text{PMe}_3)(\eta^2\text{-CSSe})$ and $\text{C}_5\text{H}_5\text{Rh}(\text{PMe}_3)(\eta^2\text{-CSSe})$[8,12]) as precursors for the preparation of (thiocarbonyl)palladium complexes.

Results

The Synthesis of $\text{Pd}(\eta^2\text{-CSSe})$ Complexes. The coordinatively unsaturated compound $\text{Pd}(\text{P-}i\text{-Pr}_3)_2$, which on treatment with CS_2 readily gives $(\text{P-}i\text{-Pr}_3)_2\text{Pd}(\eta^2\text{-CS}_2)$,[13b] also reacts with CSSe in methanol to form $(\text{P-}i\text{-Pr}_3)_2\text{Pd}(\eta^2\text{-CSSe})$ (**1**). This thiocarbonyl selenide complex is also obtained in good yield on reaction of $\text{Pd}(\text{P-}i\text{-Pr}_3)_3$ with CSSe, provided that equimolar amounts of both starting materials are used. In the presence of excess CSSe, the phosphine displaced during the formation of **1** presumably reacts with the heteroallene to produce a zwitterionic compound $\text{P-}i\text{-Pr}_3{}^+\text{CSSe}^-$ (analogous to $\text{P-}i\text{-Pr}_3{}^+\text{CS}_2{}^-$)[16] which due to its low solubility could not be completely separated from **1**.

The bis(triphenylphosphine)palladium complex **2** is obtained nearly quantitatively from $\text{Pd}(\text{PPh}_3)_4$ and CSSe. Like **1**, it forms rather air-stable crystals which are significantly soluble only in CH_2Cl_2. The IR spectrum of each

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[1] Part 11 of the series: "Complexes with Carbon Sulfides and Selenides as Ligands". Part 10: Werner, H.; Kolb, O.; Schubert, U.; Ackermann, K. *J. Organomet. Chem.* **1982**, *240*, 421.

[2] (a) Butler, I. S.; Fenster, A. E. *J. Organomet. Chem.* **1974**, *66*, 161. (b) Yaneff, P. V. *Coord. Chem. Rev.* **1977**, *23*, 183; (c) Werner, H. *Ibid.* **1982**, *43*, 165.

[3] Eisenberg, R.; Hendriksen, D. E. *Adv. Catal.* **1979**, *28*, 119.

[4] Ibers, J. A. *Chem. Soc. Rev.* **1982**, *11*, 57.

[5] Uhlig, E.; Poppitz, W. *Z. Chem.* **1979**, *19*, 191.

[6] (a) Fachinetti, G.; Biran, C.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1979**, 792. (b) Werner, H.; Heiser, B.; Burschka, Ch. *Chem. Ber.* **1982**, *115*, 3069.

[7] Herberhold, M.; Reimer, D.; Zimmer-Gasser, B.; Schubert, U. *Z. Naturforsch., B: Anorg. Chem. Org. Chem.* **1980**, *35 B*, 1281.

[8] Werner, H.; Kolb, O. *Angew. Chem.* **1979**, *91*, 930; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 865.

[9] Brothers, P. J.; Headford, C. E. L.; Roper, W. R. *J. Organomet. Chem.* **1980**, *195*, C29.

[10] Werner, H. *Pure Appl. Chem.* **1982**, *54*, 177.

[11] (a) Werner, H.; Leonhard, K.; Burschka, Ch. *J. Organomet. Chem.* **1978**, *160*, 291. (b) Werner, H.; Juthani, B. *Ibid.* **1981**, *209*, 211.

[12] Kolb, O.; Werner, H., manuscript in preparation. See: Kolb, O. Ph.D. Thesis, University of Würzburg, 1983.

[13] (a) Werner, H.; Bertleff, W. *Chem. Ber.* **1980**, *113*, 267. (b) Bertleff, W.; Werner, H. *Z. Naturforsch., B: Anorg. Chem. Org. Chem.* **1982**, *37B*, 1294.

[14] Werner, H.; Bertleff, W.; Zimmer-Gasser, B.; Schubert, U. *Chem. Ber.* **1982**, *115*, 1004.

[15] Bertleff, W.; Werner H. *Chem. Ber.* **1982**, *115*, 1012.

[16] Jensen, K. A. *J. Prakt. Chem.* **1937**, *148*, 101.

0276-7333/83/2302-0891$01.50/0

compound (in Nujol) shows two bands in the region between 1175 and 1150 cm^{-1} (Table I) which indicate the presence of a C=S double bond. Similar absorptions are observed in the spectrum of $(PPh_3)_2Pd(\eta^2\text{-}CS_2)$[17] for which the $\overline{\text{PdSC}}$ three-membered ring together with an exocyclic C=S bond has been confirmed by X-ray structural analysis.[18]

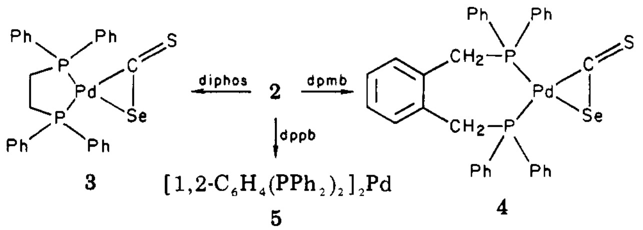
$$\underset{n\,=\,2\text{ or }3}{Pd(P\text{-}i\text{-}Pr_3)_n} \xrightarrow[-(n\,-\,2)P\text{-}i\text{-}Pr_3]{CSSe} \underset{\mathbf{1}}{(P\text{-}i\text{-}Pr_3)_2Pd(\eta^2\text{-}CSSe)}$$

$$Pd(PPh_3)_4 \xrightarrow[-2PPh_3]{CSSe} \underset{\mathbf{2}}{(PPh_3)_2Pd(\eta^2\text{-}CSSe)}$$

In contrast to $Pd(P\text{-}i\text{-}Pr_3)_n$ and $Pd(PPh_3)_4$, the corresponding compounds $Pd(PMePh_2)_4$, $Pd(PMe_2Ph)_4$, and $Pd(PMe_3)_4$ do not react with CSSe to yield products of general composition $(PR_3)_2Pd(\eta^2\text{-}CSSe)$. Instead, binuclear complexes $[(PR_3)Pd(\mu\text{-}SCSePR_3)]_2$ are obtained in 80–90% yield.[19] From the ^1H and ^{31}P NMR data,[19] there is no doubt that the structures of these compounds and of their previously described analogues $[(PR_3)Pd(\mu\text{-}SCSPR_3)]_2$ (PR_3 = PMe_3, PMe_2Ph)[13b] are almost identical. While all our attempts to obtain single crystals of $[(PR_3)Pd(\mu\text{-}SCSePR_3)]_2$ (PR_3 = PMe_3, PMe_2Ph, $PMePh_2$) failed, we are presently optimistic about one of the related binuclear complexes formed from $Pd(PR_3)_4$ andd CSe_2.[20] A definite structural assignment for $[(PR_3)Pd(\mu\text{-}SCSePR_3)]_2$, therefore, must await the completion of these studies.

Unlike $C_5H_5Co(PMe_3)(\eta^2\text{-}CSSe)$ and $C_5H_5Rh(PMe_3)(\eta^2\text{-}CSSe)$,[8,12] compounds **1** and **2** do not react with phosphines to give the desired thiocarbonyl complexes $[(PR_3)_2Pd(CS)]_n$. In reactions with PMe_3, the binuclear product $[(PMe_3)Pd(SCSePMe_3)]_2$ again is obtained instead.[19] Diphosphines such as $1,2\text{-}C_2H_4(PPh_2)_2$ (diphos) and $1,2\text{-}C_6H_4(CH_2PPh_2)_2$ (dpmb) displace the PPh_3 ligands in **2** leading to quantitative formation of the red rather air-stable chelate complexes **3** and **4**. A similar displacement reaction has already been observed with $(PPh_3)_2Pd(\eta^2\text{-}CS_2)$ and diphos to give $(diphos)Pd(\eta^2\text{-}CS_2)$ in good yields.[18]

The diphosphine $1,2\text{-}C_6H_4(PPh_2)_2$ (dppb) surprisingly reacts with **2** by substitution of both the triphenylphosphine and the heteroallene ligands. The same product **5** is also obtained from $(PPh_3)_2Pd(\eta^2\text{-}CS_2)$ and dppb.[20] Compound **5** forms dark red crystals which in contrast to the starting complex are easily soluble in benzene. The composition of **5** has been established by elemental analysis and the ^{31}P NMR spectrum.



3 $[1,2\text{-}C_6H_4(PPh_2)_2]_2Pd$ **4**

5

Table I. ^1H, ^{31}P NMR, and IR Data of 1-4

complex	^1H NMR,[a] δ	^{31}P NMR[b] δ	^{31}P NMR[b] $J(PP)$, Hz	IR[c] $\nu(CS)$, cm^{-1}
1	1.10 (dd, $PCHCH_3$)[d]	44.44 (s, br)		1175 (m), 1150 (s)
2	7.30 (m, PC_6H_5)	49.26 (s, br)		1170 (m), 1160 (s)
3	2.50 (m, CH_2)[e]	37.27 (d)	3.71	1163 (m), 1151 (s)
	7.48 (m, PC_6H_5)	38.80 (d)		
4	1.37 (m, CH_2)[e]	8.47 (d)	34.24	1160 (m), 1150 (s)
	7.50 (m, PC_6H_5 + C_6H_4)	25.50 (d)		

[a] In CH_2Cl_2. [b] 1 and 2 in CH_2Cl_2-$(CD_3)_2CO$ = 10:1; 3 and 4 in CH_2Cl_2-C_6D_6 = 10:1. [c] In Nujol. [d] Broadened signal; $J(HH) \approx 7.0$ Hz, $J(PH) \approx 14.0$ Hz; multiplet of the $PCHCH_3$ protons could not be observed. [e] Pattern corresponding to an AXX'YY'M system.

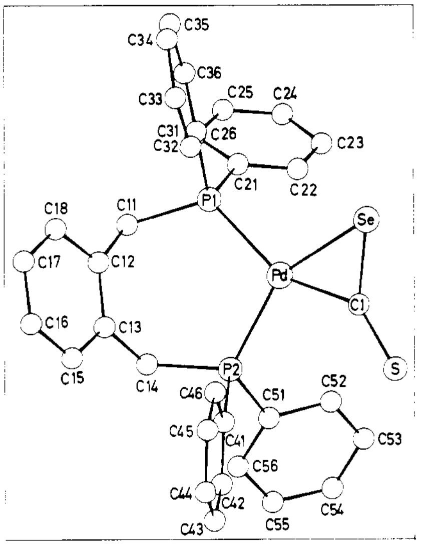


Figure 1. The molecular structure of $[1,2\text{-}C_6H_4(CH_2PPh_2)_2]Pd(\eta^2\text{-}CSSe)$ (**4**).

Experiments directed toward the preparation of single crystals of compound **3** led to an unexpected result. From CH_2Cl_2–Et_2O a dark-red microcrystalline material was obtained which correctly analyzed for (diphos)Pd(CSSe) but differs in the IR spectrum considerably from **3**. There are two characteristic bands (in Nujol) at 980 and 870 cm^{-1} pointing to the possible existence of a $Pd(\mu\text{-}CSSe)Pd$ bridging unit. Since similar complexes of general composition $L_nM(\mu\text{-}CS_2)M'L'_m$ are known to show infrared bands in the same region,[2] a dimeric structure is tentatively assigned for the new product. Studies in progress are concerned with the synthesis of the corresponding platinum compounds, of which the NMR spectra (particularly ^{31}P and ^{77}Se) should be investigated in detail.

Crystal Data and Structure Determination of 4. In contrast to our attempts with **3**, we succeeded in obtaining suitable single crystals of **4** from benzene–hexane. They are monoclinic with a = 958.5 (13) pm, b = 1502 (2) pm, c = 2150 (5) pm, β = 103.1 (2)°, and V = 3015·10^6 pm^3. The cell constants resulted from least-squares refinement of 15 reflections from different parts of the reciprocal space. The space group is $P2_1/c$ from systematic absences, d(calcd) = 1.55 g/cm^3. A total of 4291 independent reflections were collected on a Syntex $P2_1$ four-circle automatic diffractometer (MoK_α radiation, λ = 71.069 pm, graphite monochromator, ω scan, $\Delta\omega$ = 0.9°) in the range $2° \leq 2\theta \leq 47°$. Corrections for absorption (μ_{Mo} = 21.0 cm^{-1}) and extinctions were not applied. The structure was solved by the Patterson method (Syntex XTL). The hydrogen positions were calculated according to ideal geometry. Refinement of the non-hydrogen atoms by full-matrix

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[17] Baird, M. C.; Wilkinson, G. *J. Chem. Soc. A* **1967**, 855.

[18] Kashiwagi, T.; Yasuoka, N.; Ueki, T.; Kasai, N.; Kakudo, M.; Takahashi, S.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 296.

[19] Bertleff, W. Ph.D Thesis, University of Würzburg, 1981.

[20] Ebner, M., unpublished results.

Table II. Positional and Thermal Parameters and their Estimated Standard Deviations for 4[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pd	0.1463 (2)	0.24323 (9)	0.15575 (6)	2.93 (6)	3.29 (7)	3.03 (6)	0.76 (7)	0.53 (4)	0.19 (7)
Se	0.2785 (3)	0.1076 (1)	0.1866 (1)	5.9 (1)	4.5 (1)	5.8 (1)	2.1 (1)	1.4 (1)	0.6 (1)
C(1)	0.200 (2)	0.175 (1)	0.2384 (8)	3.2 (9)	3.2 (9)	4.6 (10)	0.3 (8)	−0.9 (8)	0.2 (8)
S	0.1820 (7)	0.1794 (4)	0.3113 (3)	8.5 (4)	5.9 (3)	3.9 (3)	0.8 (3)	1.6 (3)	0.5 (3)
C(11)	0.088 (2)	0.381 (1)	0.0139 (8)	5.6 (12)	4.2 (10)	3.1 (9)	1.8 (10)	0.9 (9)	1.3 (8)
C(12)	0.168 (3)	0.450 (2)	0.055 (1)	6.3 (15)	5.3 (13)	5.6 (14)	2.2 (12)	2.5 (12)	1.7 (11)
C(13)	0.128 (2)	0.489 (1)	0.106 (1)	5.9 (14)	4.5 (12)	4.4 (11)	1.3 (11)	0.6 (11)	1.3 (10)
C(14)	−0.003 (2)	0.457 (1)	0.1267 (9)	4.2 (11)	4.6 (10)	4.9 (11)	0.9 (9)	2.6 (9)	0.9 (8)
C(15)	0.213 (3)	0.557 (2)	0.141 (1)	7.5 (16)	4.8 (12)	7.4 (15)	0.2 (12)	2.6 (13)	0.3 (11)
C(16)	0.333 (3)	0.588 (18)	0.121 (1)	5.5 (17)	6.4 (17)	19.5 (30)	−2.1 (14)	5.0 (18)	−2.1 (18)
C(17)	0.375 (3)	0.552 (2)	0.071 (2)	6.5 (19)	6.1 (17)	24.0 (39)	−0.6 (14)	8.3 (22)	−3.0 (20)
C(18)	0.297 (3)	0.485 (2)	0.037 (1)	8.7 (19)	5.9 (15)	7.5 (16)	1.8 (14)	3.9 (15)	2.4 (12)
P(1)	0.1323 (5)	0.2685 (3)	0.0459 (2)	3.6 (3)	4.6 (3)	3.0 (2)	1.2 (2)	0.6 (2)	0.0 (2)
P(2)	0.0321 (5)	0.3648 (3)	0.1844 (2)	3.1 (3)	3.8 (3)	3.2 (2)	0.6 (2)	1.1 (2)	0.3 (2)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(21)	0.001 (2)	0.198 (1)	−0.0067 (9)	4.2 (4)	C(31)	0.303 (2)	0.245 (1)	0.0235 (8)	3.7 (3)
C(22)	−0.050 (2)	0.127 (1)	0.015 (1)	6.1 (5)	C(32)	0.420 (2)	0.272 (1)	0.0662 (9)	6.4 (5)
C(23)	−0.153 (3)	0.072 (2)	−0.024 (1)	7.7 (6)	C(33)	0.555 (3)	0.263 (2)	0.050 (1)	7.9 (6)
C(24)	−0.200 (2)	0.093 (2)	−0.084 (1)	6.6 (6)	C(34)	0.567 (3)	0.229 (2)	−0.004 (1)	8.0 (6)
C(25)	−0.160 (3)	0.163 (2)	−0.108 (1)	8.8 (7)	C(35)	0.446 (3)	0.206 (2)	−0.049 (1)	9.6 (8)
C(26)	−0.060 (3)	0.223 (2)	−0.072 (1)	7.4 (6)	C(36)	0.311 (3)	0.216 (2)	−0.033 (1)	7.7 (6)
C(41)	0.135 (2)	0.420 (1)	0.2569 (8)	4.2 (4)	C(51)	−0.143 (2)	0.343 (1)	0.2013 (7)	3.6 (4)
C(42)	0.075 (3)	0.466 (2)	0.296 (1)	7.7 (6)	C(52)	−0.176 (2)	0.255 (1)	0.2100 (8)	5.1 (4)
C(43)	0.164 (4)	0.508 (2)	0.349 (1)	10.9 (8)	C(53)	−0.309 (2)	0.234 (1)	0.2248 (9)	5.6 (5)
C(44)	0.306 (3)	0.508 (2)	0.358 (1)	8.5 (7)	C(54)	−0.404 (2)	0.301 (1)	0.2275 (9)	5.3 (5)
C(45)	0.365 (3)	0.463 (2)	0.318 (1)	7.0 (6)	C(55)	−0.374 (2)	0.385 (1)	0.2170 (8)	4.5 (4)
C(46)	0.278 (3)	0.419 (1)	0.264 (1)	6.9 (6)	C(56)	−0.243 (2)	0.409 (1)	0.2020 (8)	4.3 (4)

atom[b]	x	y	z	atom	x	y	z
H(22)	−0.012	0.111	0.060	H(32)	0.410	0.299	0.107
H(23)	−0.191	0.019	−0.007	H(33)	0.641	0.284	0.081
H(24)	−0.268	0.054	−0.112	H(34)	0.662	0.219	−0.013
H(25)	−0.202	0.178	−0.153	H(35)	0.456	0.188	−0.092
H(26)	−0.032	0.279	−0.091	H(36)	0.223	0.199	−0.065
H(42)	−0.030	0.468	0.288	H(52)	−0.108	0.206	0.207
H(43)	0.118	0.541	0.379	H(53)	−0.338	0.172	0.231
H(44)	0.366	0.542	0.394	H(54)	−0.496	0.287	0.239
H(45)	0.469	0.456	0.328	H(55)	−0.445	0.432	0.220
H(46)	0.324	0.387	0.233	H(56)	−0.223	0.472	0.193
H(111)	−0.014	0.391	0.008	H(141)	−0.044	0.507	0.146
H(112)	0.106	0.385	−0.029	H(142)	−0.075	0.440	0.090
H(15)	0.185	0.583	0.178	H(17)	0.459	0.577	0.057
H(16)	0.393	0.633	0.149	H(18)	0.328	0.458	0.000

[a] The form of the anisotropic thermal parameter is $\exp[-1/4(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$; B_{ij} in 10^4 pm^2. [b] Hydrogen atoms, B = 7.0 Å^2.

Table III. Selected Bond Distances (pm) and Bond Angles (deg) with Estimated Standard Deviations

Bond Distances

Pd-C(1)	201 (2)	C(1)-S	162 (2)	P(2)-C(41)	184 (2)
Pd-P(1)	236.6 (5)	P(1)-C(11)	184 (2)	P(2)-C(51)	183 (2)
Pd-P(2)	228.3 (5)	P(1)-C(21)	182 (2)	C(11)-C(12)	146 (3)
Pd-Se	241.2 (3)	P(1)-C(31)	184 (2)	C(12)-C(13)	138 (3)
C(1)-Se	180 (2)	P(2)-C(14)	184 (2)	C(13)-C(14)	150 (3)

Bond Angles

P(1)-Pd-P(2)	102.6 (2)	Pd-C(1)-S	140.9 (11)	Pd-P(2)-C(14)	116.6 (6)
P(1)-Pd-Se	108.5 (1)	Pd-C(1)-Se	78.4 (7)	Pd-P(2)-C(41)	113.1 (6)
P(2)-Pd-C(1)	102.1 (5)	Pd-P(1)-C(11)	118.4 (6)	Pd-P(2)-C(51)	115.3 (6)
C(1)-Pd-Se	46.8 (5)	Pd-P(1)-C(21)	113.7 (6)	P(1)-C(11)-C(12)	112.2 (15)
Se-C(1)-S	140.7 (11)	Pd-P(1)-C(31)	112.2 (6)	P(2)-C(14)-C(13)	113.3 (14)

least-squares resulted in R_1 = 0.088 and R_2 = 0.079 for 2315 structure factors with $F_o \geq 4\sigma(F_o)$. Structure factors for uncharged atoms according to International Tables of Crystallography were used, corrected for anomalous dispersion. The final atomic coordinates are listed in Table II and selected intramolecular bond lengths and angles in Table III. The molecular structure is shown in Figure 1.

The molecular structure of 4, which to the best of our knowledge is the first structurally characterized transition-metal CSSe complex, is shown in Figure 1. The most remarkable features are, first, the coordination of the thiocarbonyl selenide via C and Se to the palladium and, second, the significant difference in the Pd–P distances which are 228.3 (5) (trans to Se) and 236.6 (5) pm (trans to C). A similar difference reflecting the characteristic trans-lengthening effect of the carbon atom has been observed for $(PPh_3)_2Pd(\eta^2\text{-}CS_2)$ where the Pd–P distances are 231.6 and 241.5 pm, respectively.[18] The four atoms linked to palladium in 4 are approximately in one plane, the dihedral angle between the P(1)–Pd–P(2) and the C(1)–Pd–Se planes being 3°. The seven-membered ring adopts boat conformation such that the dihedral angle between the P(1), C(11), P(2), C(14) plane and the plane of the phenylene moiety is 68° and between the former plane and the P(1), Pd, P(2) plane is 13°. With this kind of puckering, the phenylene plane and the plane of coordination around the Pd atom are nearly perpendicular (81°).

The bending of the heteroallene fragment in 4 is very similar to that found in transition-metal CS_2 complexes. Whereas the S–C–S angles in $(PPh_3)_2Pd(\eta^2\text{-}CS_2)$,[18] $(PPh_3)_2Pt(\eta^2\text{-}CS_2)$,[21] and $C_5H_5Co(PMe_3)(\eta^2\text{-}CS_2)$[11a] are 140, 136.2, and 141.2°, the corresponding S–C–Se angle in 4 is 141 (1)°. Also the degree of lengthening of the two carbon–chalcogen bonds brought about by the coordination of the heteroallene to the metal is quite comparable. In $(PPh_3)_2Pd(\eta^2\text{-}CS_2)$ the two C–S distances are 165 (coordinated S) and 163 pm (compared with 155.4 pm in free CS_2), while in 4 the C–Se and C–S bond lengths are 180 (2) and 162 (2) pm, respectively (compared with 170.9 and 155.7 pm in free CSSe, values estimated from microwave data).[22] The distinct lengthening of these bonds supports the argument that the carbon dichalogenides CEE′ (E, E′ = S or Se) have good π-acceptor properties.[2,23]

Discussion

The present investigations have shown that there is a strong similarity in the behavior of CS_2 and CSSe toward (phosphine)palladium(0) complexes. While $Pd(P\text{-}i\text{-}Pr_3)_n$ (n = 2 or 3) and $Pd(PPh_3)_4$ react with both heteroallenes to yield mononuclear products $(PR_3)_2Pd(\eta^2\text{-}CSE)$ (E = S or Se), in the reactions of $Pd(PMe_3)_4$ and $Pd(PMe_2Ph)_4$ with CS_2 and CSSe, binuclear compounds (presumably containing the corresponding zwitterions $PR_3^+CSE^-$ as a bridging unit) are obtained.

In addition, the reactivities of the complexes $(PR_3)_2Pd(\eta^2\text{-}CS_2)$ and $(PR_3)_2Pd(\eta^2\text{-}CSSe)$ (R = i-Pr, Ph) toward mono- and bidentate phosphines are almost analogous. There is no evidence that on treatment with PMe_3, PPh_3, or P-c-Hx_3 these compounds yield palladium thiocarbonyls. The complexes containing PPh_3 as ligand cleanly react with the diphosphines diphos and dpmb to produce (diphos)$Pd(\eta^2\text{-}CSE)$ and (dpmb)$Pd(\eta^2\text{-}CSE)$, respectively. These chelate compounds even with E = Se are completely inert toward abstraction of a chalcogen atom, demonstrating once more the fundamental difference in the behavior between d^8 systems such as $C_5H_5M(PR_3)(\eta^2\text{-}CSSe)$ (M = Co, Rh) and d^{10} systems such as $(P\text{–}P)M(\eta^2\text{-}CSSe)$ (M = Pd, Pt).[2c,20]

The most important result of our studies is, however, that thiocarbonyl selenide—at least with palladium(0) as the central atom—prefers to coordinate in a η^2 mode via C and Se and not via C and S. According to the IR spectrum, this also seems to be true for the nickel complex (bpy)$Ni(\eta^2\text{-}CSSe)$.[24] By comparing the infrared data of 1–4 (Table I), there is no doubt that in all of these compounds the same type of coordination of CSSe is present. If the heteroallene would be linked to the metal via C and S, a strong absorption near 1000 cm^{-1} indicative of an exocyclic C=Se bond should be observed in the IR spectrum as is found for the palladium CSe_2 complexes $(PPh_3)_2Pd(\eta^2\text{-}CSe_2)$, (diphos)$Pd(\eta^2\text{-}CSe_2)$, and (dpmb)$Pd(\eta^2\text{-}CSe_2)$.[20] The reason why CSSe tends to coordinate preferably via C and Se possibly is that selenium is somewhat less electronegative than sulfur,[25] i.e., it is softer and therefore favors the η^2-C,Se- and not the η^2-C,S-bonding mode to the soft Pd(0) center.

That in 1–4 a rigid type of structure with a η^2 linkage of the thiocarbonyl selenide is present not only in the crystal but also in solution is indicated by the ^{31}P NMR data (Table I). In the spectra of 3 and 4, two doublets are observed corresponding to an AM (or AX)[26] system. The spectra of 1 and 2 show a broadened singlet which probably means that the difference in chemical shift of the two expected signals is too small to be resolved under the experimental conditions. Similar observations have been made with the carbon disulfide complexes $(PR_3)_2Pd(\eta^2\text{-}CS_2)$ (R = i-Pr, Ph).[13b] The shape of the broadened signal does not change at higher or lower temperatures, and, therefore, a fluctional structure (as found in $C_5H_5Mn(CO)_2(CS_2)$[27]) can be excluded. There is firm evidence that in the complexes $(PPh_3)_2Pt(\eta^2\text{-}CS_2)$[28] and $C_5H_5Co(PMe_2Ph)(\eta^2\text{-}CS_2)$[12] as well as in the C,S- and C,Se-bonded isomers of $Os(\eta^2\text{-}CSSe)(CO)(CN\text{-}p\text{-}tol)(PPh_3)_2$ also a rigid metal–heteroallene unit exists.

Experimental Section

NMR spectra were recorded on a Varian T 60 (^1H) and a Bruker WH 90-FT (^{31}P) and IR spectra on a Perkin-Elmer 457. The starting materials $Pd(P\text{-}i\text{-}Pr_3)_n$,[29] $Pd(PPh_3)_4$,[29,30] and CSSe[19,31] were prepared by published methods. All reactions were carried out under purified nitrogen.

Preparation of $(P\text{-}i\text{-}Pr_3)_2Pd(\eta^2\text{-}CSSe)$ (1). A solution of $Pd(P\text{-}i\text{-}Pr_3)_2$ (0.427 g, 1.0 mmol) in 5 mL of methanol was cooled to −20 °C and treated dropwise with an equimolar amount of CSSe. After vigorous stirring for 2–3 min, the resulting brown precipitate was filtered off, repeatedly washed with small amounts of cold (−50 °C) methanol, and dried in vacuo; yield 0.31 g (56%). Anal. Calcd for $C_{19}H_{42}P_2PdSSe$: C, 41.50; H, 7.64; Pd, 19.36. Found: C, 40.94; H, 7.72; Pd, 18.87.

Preparation of $(PPh_3)_2Pd(\eta^2\text{-}CSSe)$ (2). A solution of $Pd(PPh_3)_4$ (0.72 g, 0.62 mmol) in 15 mL of ether was treated dropwise with a slight excess of CSSe (0.04 mL, 0.75 mmol). After being stirred for 10 min, the solution was concentrated to about one-third of the original volume and the orange-brown precipitate filtered off. It was repeatedly washed with hexane and dried in vacuo; yield 0.46 g (97%). Anal. Calcd for $C_{37}H_{30}P_2PdSSe$: C, 59.94; H, 4.01; Pd, 14.11; S, 4.25; Se, 10.47. Found: C, 59.37; H, 4.29; Pd, 13.88; S, 4.42; Se, 10.35.

Preparation of (diphos)$Pd(\eta^2\text{-}CSSe)$ (3). To a suspension of 2 (0.50 g, 0.66 mmol) in 20 mL of hexane was added diphos (0.264 g, 0.66 mmol) with vigorous stirring. After continuous stirring for 1 h, the dark red precipitate was separated, washed twice with ether and hexane, and dried in vacuo: yield 0.36 g (87%); mp 208 °C dec (DTA). Anal. Calcd for $C_{27}H_{24}P_2PdSSe$: C, 51.65; H, 3.85; Pd, 16.94. Found: C, 51.66; H, 4.24; Pd, 16.02.

Preparation of (dpmb)$Pd(\eta^2\text{-}CSSe)$ (4). To a suspension of 2 (0.526 g, 0.70 mmol) in 25 mL of ether was added dpmb (0.34 g, 0.70 mmol) with vigorous stirring. After continuous stirring for 3 h, the violet precipitate was separated, washed twice with ether and hexane, and dried in vacuo; yield 0.48 g (97%). Anal. Calcd for $C_{33}H_{28}P_2PdSSe$: C, 56.29; H, 4.00; Pd, 15.11. Found: C, 55.86; H, 4.04; Pd, 15.07.

Preparation of $Pd(dppb)_2$ (5). To a suspension of 2 (0.50 g, 0.66 mmol) in 20 mL of hexane was added dppb (0.294 g, 0.66 mmol) under vigorous stirring. After continuous stirring for 1 h, the red-brown precipitate was separated and washed with ether

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(21) Mason, R.; Rae, A. I. M. *J. Chem. Soc. A* **1970**, 1767.

(22) (a) Wentink, T., Jr. *J. Chem. Phys.* **1959**, *30*, 105. (b) Frost, D. C.; Lee, S. T.; McDowell, C. A. *J. Chem. Phys.* **1973**, *59*, 5484.

(23) Herberhold, M.; Süss-Fink, M. *Angew. Chem.* **1977**, *89*, 192; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 194.

(24) Poppitz, W.; Uhlig, E. *Z. Anorg. Allg. Chem.* **1982**, *489*, 67.

(25) Wiberg, E.; Hollemann, A. F. "Lehrbuch der Anorganischen Chemie"; Verlag Walter de Gruyter; Berlin-New York, 1976; pp 122.

(26) Günter, H. "NMR-Spektroskopie"; Verlag Thieme, Stuttgart, 1973; pp 156, 164.

(27) Herberhold, M.; Süss-Fink, M.; Kreiter, C. G. *Angew. Chem.* **1977**, *89*, 191; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 193.

(28) Vergamini, P. J.; Eller, P. G. *Inorg. Chim. Acta* **1979**, *34*, L 291.

(29) Kuran, W.; Musco, A. *Inorg. Chim. Acta* **1975**, *12*, 187.

(30) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.

(31) Markovskii, L.; Vekshina, M.; Voevodskaya, T. *Zh. Prikl. Kim.* **1970**, *43*, 5.

and hexane. It was then dissolved in 15 mL of benzene and the solution was filtered. Addition of hexane and cooling to 0° C gave dark red crystals: yield 0.3 g (45%); 210 °C dec (DTA); ^{31}P NMR (C_6D_6) δ 32.06 (s). Anal. Calcd for $C_{60}H_{48}P_4Pd$: C, 72.10; H, 4.84; Pd, 10.64. Found: C, 72.04; H, 4.95; Pd, 10.45.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support and BASF and DEGUSSA for gifts of chemicals. We also thank Mrs. M. Rothenburger, U. Neumann, and R. Schedl for the elemental analysis, Mr. C. P. Kneis for the ^{31}P NMR spectra, Mr. J. Riede for measurements at the diffractometer, and Dr. W. Buchner for valuable discussions.

Registry No. 1, 85318-45-2; 2, 85318-46-3; 3, 85318-47-4; 4, 85318-48-5; 5, 85318-49-6.

Supplementary Material Available: Listing of the structure factors for 4 (20 pages). Ordering information is given on any current masthead page.

Reactions of Nickel Atoms with Substituted Ethylenes

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Received November 23, 1982

Nickel atoms have been codeposited with substituted ethylenes at −196 °C in an attempt to synthesize new organometallics capable of depositing metallic films at moderate temperatures. Thermally unstable homoleptic nickel–olefin complexes with the stoichiometry Ni(olefin)$_3$ were formed, but not isolated. Reaction of these complexes with trifluorophosphine at low temperatures led to the partial displacement of olefin and the isolation and characterization of three new $(PF_3)_3$Ni(olefin) compounds. The $(PF_3)_3$Ni(olefin) compounds were found to decompose between −16 and +6 °C to give $Ni(PF_3)_4$, olefin, and nickel metal.

The decomposition of organometallic compounds by pyrolytic[1] and photolytic[2,3] techniques has received considerable attention as a method of depositing metallic films. Both of these approaches have inherent disadvantages associated with the inclusion of impurities in either the film structure, the substrate, or both. We have recently been interested in the synthesis of new organometallics with moderate thermal stability that can be decomposed controllably at relatively low temperatures (e.g., below 100 °C) to produce metallic films. This paper describes our attempt to use the metal-vapor technique to synthesize such compounds containing nickel.

The importance of metal-vapor chemistry in organometallic syntheses has been discussed in detail in recent review articles.[4,5] In addition to its direct synthetic utility, it has also been combined with matrix isolation techniques in spectroscopic studies to suggest new, potentially fruitful areas for synthesis work. For example, the low-temperature optical spectra of homoleptic nickel–olefin complexes have led Ozin and Power to propose that such complexes might be stable enough for macroscale syntheses.[6] We have investigated some of these systems further to determine their suitability as synthetic reactions.

Experimental Section

General Data. The metal-atom vapor apparatus is similar to that described in detail elsewhere.[7] Vacuum system manipulations were carried out in a Pyrex system with greaseless Kontes glass/Teflon valves. Routine infrared spectra were recorded on a Perkin-Elmer 457 spectrometer using a 5-cm glass cell with KBr windows. Attempts to obtain infrared spectra of isolable, but thermally unstable, products were made by using a Digilab FTS-15C Fourier transform interferometer. NMR spectra were recorded on a Varian EM-390 spectrometer operating at 90 MHz for proton and 84.68 MHz for fluorine nuclei and equipped with an EM-3940 variable-temperature accessory calibrated with a methanol sample.

Propene, vinyl chloride, and vinyl fluoride were obtained from Matheson Gas Products and used as received. Trifluoropropene, fluorobenzene, trifluoromethylbenzene, *m*-bis(trifluoromethyl)benzene, and hexafluorobenzene were purchased from PCR and used without further purification. The arenes were stored under vacuum over activated 4A molecular sieves. Trifluorophosphine was obtained from Ozark-Mahoning and purified by vacuum distillation through a −160 °C trap.

Reactions of Ni Atoms with Olefins. The same general procedure was followed in all reactions of nickel atoms with olefins and will be described in detail for the reaction with trifluoropropene. Nickel metal (6.27 mmol) was vaporized under a dynamic vacuum from a tungsten/alumina crucible and codeposited over 1.75 h with trifluoropropene (47.38 mmol) at liquid-nitrogen temperatures to form a dark brown matrix. At this point, the reactor was closed off and the liquid nitrogen removed to allow gradual warming. When the matrix melted, streaks of brown liquid collected in the bottom of the reactor which was then immersed in a toluene slush bath at −96 °C. After 15 min, the reactor was opened to a trap at liquid-nitrogen temperatures, and the volatile material was collected during a 1.25 h period. The −96 °C bath was then removed and the reactor allowed to warm gradually to ambient temperatures with any remaining volatile materials bring collected in a separate trap at −196 °C. The volatile materials collected at −96 °C (35.88 mmol) and between −96 °C and ambient (10.37 mmol) were identified as trifluoropropene.

Synthesis of $(PF_3)_3Ni(FCH{=}CH_2)$. The reaction of nickel vapor with $FCH{=}CH_2$ and PF_3 described here was representative of those reactions involving other olefins. Nickel metal (2.79 mmol) was vaporized and codeposited with $FCH{=}CH_2$ (41.53 mmol) at liquid-nitrogen temperatures during 1.5 h. The reactor was closed off and the dark brown matrix warmed slightly until it melted producing streaks of brown liquid that collected at the

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(1) Domrachev, G. A.; Suvorova, O. *N. Uspekhi Khim.* **1980**, *49*, 1671 (*Russ. Chem. Rev.* **1980**, *49*, 810).

(2) George, P. M.; Beauchamp, J. L. *Thin Solid Films* **1980**, *67*, L25.

(3) Ehrlich, D. J.; Osgood, R. M., Jr.; Deutsch, T. F. *J. Electrochem. Soc.* **1981**, *128*, 2039.

(4) Klabunde, K. J. *Acc. Chem. Res.* **1975**, *8*, 393.

(5) Timms, P. L.; Turney, T. W. Adv. *Organomet. Chem.* **1977**, *15*, 53.

(6) Ozin, G. A.; Power, W. J. *Inorg. Chem.* **1978**, *17*, 2836.

(7) Klabunde, K. J.; Timms, P. L.; Skell, P. S.; Ittel, S. *Inorg. Synth.* **1979**, *19*, 59.