Coordination Chemistry Reviews, 43 (1982) 165–185
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

NOVEL COORDINATION COMPOUNDS FORMED FROM CS_2 AND HETEROALLENES

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A. INTRODUCTION

The interest in the coordination chemistry of CS_2 and similar heteroallenes with transition metals stems from the fact that these small molecules are structurally related to carbon dioxide and thus their metal complexes may be regarded as model compounds for CO_2 activation. Research to date clearly indicates that CO_2 is a poor ligand and only shows a low tendency to coordinate to transition metal centers. It seems that new strategies are necessary to prepare and isolate stable carbon dioxide–metal complexes.

In contrast to CO_2, carbon disulfide possesses rather favorable coordinating properties, in particular to low valent transition metals containing phosphines or phosphites as further ligands. In 1966, the work of Baird and Wilkinson opened the gate to the chemistry of CS_2 metal complexes [1]. These authors found that $Pt(PPh_3)_3$ undergoes a rapid and quantitative reaction with CS_2 under mild conditions to produce the compound

0010-8545/82/0000-0000/$05.25

$Pt(PPh_3)_2(CS_2)$, which, according to the X-ray analysis [2], contains a three-membered ring with Pt–C and Pt–S bonds. Carbon disulfide, therefore, behaves like an alkene or alkine, i.e. a *dihapto*-bonded (η^2) ligand. In further studies, Baird and Wilkinson also observed [3] that the triphenylphosphine complexes of palladium, rhodium and iridium react smoothly with CS_2 to yield products in which the carbon disulfide is coordinated in the same way as in the before-mentioned platinum complex $Pt(PPh_3)_2(\eta^2\text{-}CS_2)$. The rhodium compound $Rh(PPh_3)_2(\eta^2\text{-}CS_2)(\eta^1\text{-}CS_2)Cl$, obtained from "Wilkinson's catalyst" $Rh(PPh_3)_3Cl$ and CS_2, is rather unstable and is formed as an intermediate in the synthesis of $Rh(PPh_3)_2(CS)Cl$, the first fully characterized metal thiocarbonyl complex [4].

It was mainly this result which further stimulated the interest in the coordinating properties of CS_2. To date, there are certainly more than one hundred carbon disulfide–metal complexes described in the literature and there are at least two previous review articles [5,6] summarizing the state-of-the-art in this field.

Among the various methods of preparation of these complexes there seems to be one common feature. A bond between the metal atom and the CS_2 molecule is preferentially formed when the starting compound contains a nucleophilic metal center, i.e. when the original metal complex behaves like a Lewis base. The triphenylphosphineplatinum(0), -palladium(0), -rhodium(I) and -iridium(I) compounds are striking examples of this type of complex as it is well known [7] that they readily react with various electrophilic substrates (e.g. HX, MeI, MeCOCl, etc.) by oxidative addition. CS_2 and heteroallenes such as COS, SCNR, OCNR, RNCNR, etc. also behave as electrophiles. Their $\delta+$ charged central carbon atom can be attacked not only by conventional nucleophiles (e.g. OR^-, SR^-, NHR^-, etc.) but also by metallic bases to form a primary compound containing a metal-to-carbon bond. Whether this compound is stable or not, is mainly determined by the energetics of subsequent reactions, e.g. the formation of metal thiocarbonyls from CS_2 and metal phosphine complexes. The lability of $Rh(PPh_3)_2(\eta^2\text{-}CS_2)(\eta^1\text{-}CS_2)Cl$ and the inertness of $Pt(PPh_3)_2(\eta^2\text{-}CS_2)$ may illustrate the different behavior of structurally similar compounds.

Our own work in this field primarily originated from interest in the chemistry of half-sandwich type complexes $C_5H_5ML_2$ (M = Co, Rh, Ir). During studies concerned with the reactivity of the bis(phosphite) complexes (in particular with $L = P(OMe)_3$ and $P(OEt)_3$ [8]), it was learned that these d^8 systems react with electrophiles such as HBF_4 or MeI to form stable cations containing a M–H or M–CH_3 bond [9]. The bis(trialkylphosphine) compounds, e.g. $C_5H_5Co(PMe_3)_2$ [10] and $C_5H_5Rh(PMe_3)_2$ [11], are even more nucleophilic and attacked not only by weak Brönsted acids such as NH_4^+ or MeOH but also by Me_3GeCl, Ph_3SnCl, $SnCl_4$, $ZnCl_2$, etc. Would the basicity of the metal be strong enough to allow similar reactions to occur with CS_2 and heteroallenes?

Besides the cobalt and rhodium complexes interest was also shown in the nucleophilic behavior of palladium(0) phosphine compounds, e.g. $Pd(PMe_3)_4$ and $Pd(PPr^i_3)_3$ [12], and thus it was intended to compare the reactivity of this type of metallic bases with that of $C_5H_5Co(PR_3)_2$ and $C_5H_5Rh(PR_3)_2$. Would the trialkylphosphine palladium complexes behave analogously to $Pd(PPh_3)_4$, already used by Baird and Wilkinson for reactions with CS_2 [3]? And would these $Pd(PR_3)_n$ complexes also react with other heteroallenes?

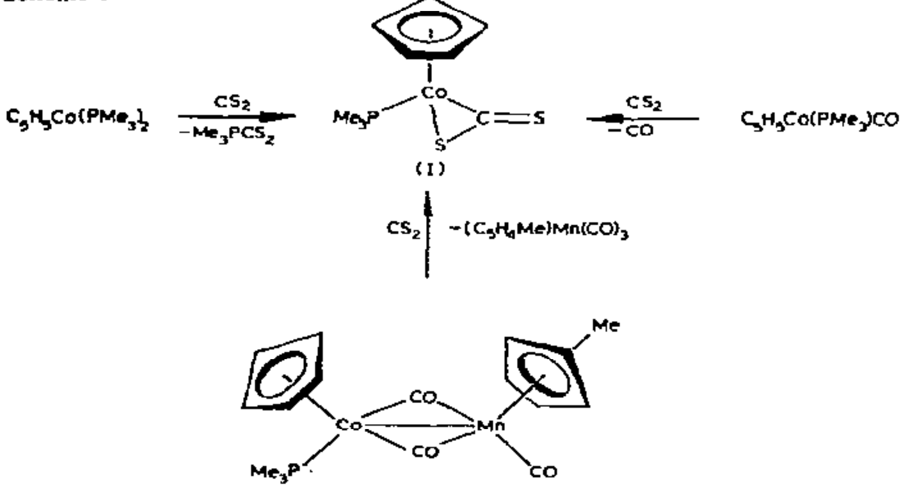
This brief review summarizes some answers to these questions.

B. COBALT AND RHODIUM COMPLEXES

(i) Complexes obtained from CS_2: structure and reactivity of the compounds $C_5H_5M(PMe_3)(\eta^2\text{-}CS_2)$

The bis(trimethylphosphine) complexes $C_5H_5Co(PMe_3)_2$ and $C_5H_5Rh(PMe_3)_2$ react with CS_2 at room temperature to give the air-stable compounds $C_5H_5Co(PMe_3)(\eta^2\text{-}CS_2)$ (**I**) [13] and $C_5H_5Rh(PMe_3)(\eta^2\text{-}CS_2)$ (**II**) [14]. The cobalt complex (**I**) is also obtained from $C_5H_5Co(PMe_3)CO$ and CS_2 [15] or on displacement of the molecule $(C_5H_4Me)Mn(CO)_3$ by CS_2 from the binuclear compound $C_5H_5(PMe_3)Co(\mu\text{-}CO)_2Mn(CO)C_5H_4Me$ [16] (Scheme 1).

Scheme 1



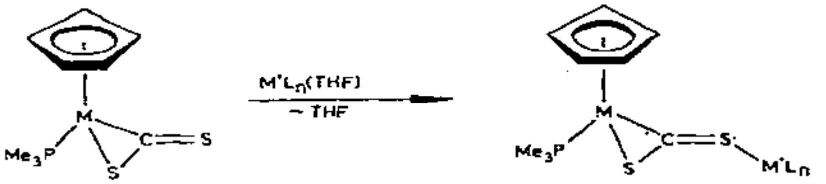
Complex (**II**) is accessible not only from $C_5H_5Rh(PMe_3)_2$ but also in much better yields from $C_5H_5Rh(PMe_3)C_2H_4$ and CS_2 by ethylene displacement [14]. The observation that contrary to our expectation $C_5H_5Rh(PMe_3)_2$

is not the most useful starting material to form (**II**) corresponds with Yamazaki's result that the analogous triphenylphosphine complex $C_5H_5Rh(PPh_3)(\eta^2\text{-}CS_2)$ is only formed in moderate yields from $C_5H_5Rh(PPh_3)_2$ and CS_2 [17].

The X-ray structure of (**I**) shows that the CS_2 molecule bonds as a *dihapto* ligand through the carbon and one sulfur atom [13]. The S–C–S angle of 141.2° is very similar to that in $Pt(PPh_3)_2(\eta^2\text{-}CS_2)$ [2]. Both C–S bond lengths in (**I**) are significantly longer than in free carbon disulfide, a result which supports the assumption that in the bonding between transition metals and CS_2 the antibonding molecular orbitals of CS_2 are significantly involved [18]. Also the spectroscopic data of the complexes (**I**) and (**II**) indicate that carbon disulfide is a good π-acceptor ligand.

The question whether the CS_2 molecule in complexes of the general type $C_5H_5M(PR_3)(\eta^2\text{-}CS_2)$ is rigid or rotating around the axis passing through the C–S bond could be answered by the NMR data of $C_5H_5Rh(PMe_2Ph)(\eta^2\text{-}CS_2)$ [14]. When the CS_2 ligand is rigid, the rhodium atom is a center of chirality and thus the methyl groups of the prochiral phosphine must give two signals in the ^1H NMR spectrum. Between −64 and +51°C this proved to be the case. There is also evidence that in the above-mentioned platinum complex $Pt(PPh_3)_2(\eta^2\text{-}CS_2)$ the $Pt\text{–}CS_2$ unit is rigid [19] whereas in $C_5H_5Mn(CO)_2CS_2$ a hindered rotation about the bonding axis occurs [20].

The complexes (**I**) and (**II**) are completely inert towards PMe_3 or PPh_3 and do not react in the well-established manner to the corresponding thiocarbonyls $C_5H_5M(PMe_3)CS$. The CS_2 complexes react, however, with $Cr(CO)_5THF$ and $C_5H_5Mn(CO)_2THF$ to yield the binuclear compounds (**III**)–(**VI**) in which the carbon disulfide bridges two different metal atoms [13,14]. The donating properties of the exocyclic sulfur atom in $C_5H_5M(PMe_3)(\eta^2\text{-}CS_2)$ seem to be rather strong as the CO stretching frequencies of, for example, (**III**) and $Cr(CO)_5PMe_3$, are nearly identical.



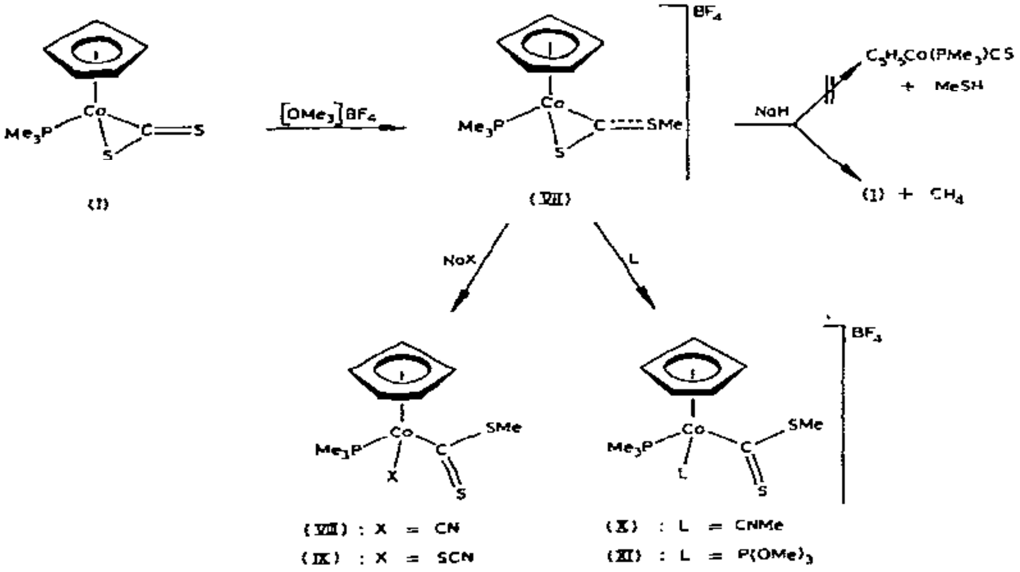
(I, II)

(III): M = Co, $M'L_n = Cr(CO)_5$
(IV): M = Co, $M'L_n = Mn(CO)_2C_5H_5$
(V): M = Rh, $M'L_n = Cr(CO)_5$
(VI): M = Rh, $M'L_n = Mn(CO)_2C_5H_5$

The nucleophilic behavior of the η^2-coordinated CS_2 ligand in (**I**) has also been demonstrated by the reaction with $[OMe_3]BF_4$ to give $[C_5H_5Co(PMe_3)(\eta^2\text{-}CS_2Me)]BF_4$ (**VII**) [21]. This salt-like compound was considered to be a second possible starting material for the preparation of $C_5H_5Co(PMe_3)CS$ since Roper and co-workers recently reported [22] that the osmium complex $[Os(CO)_2(PPh_3)_2(\eta^2\text{-}CS_2Me)]BF_4$ reacts with NaH to form the thiocarbonyl $Os(CO)_2(PPh_3)_2CS$.

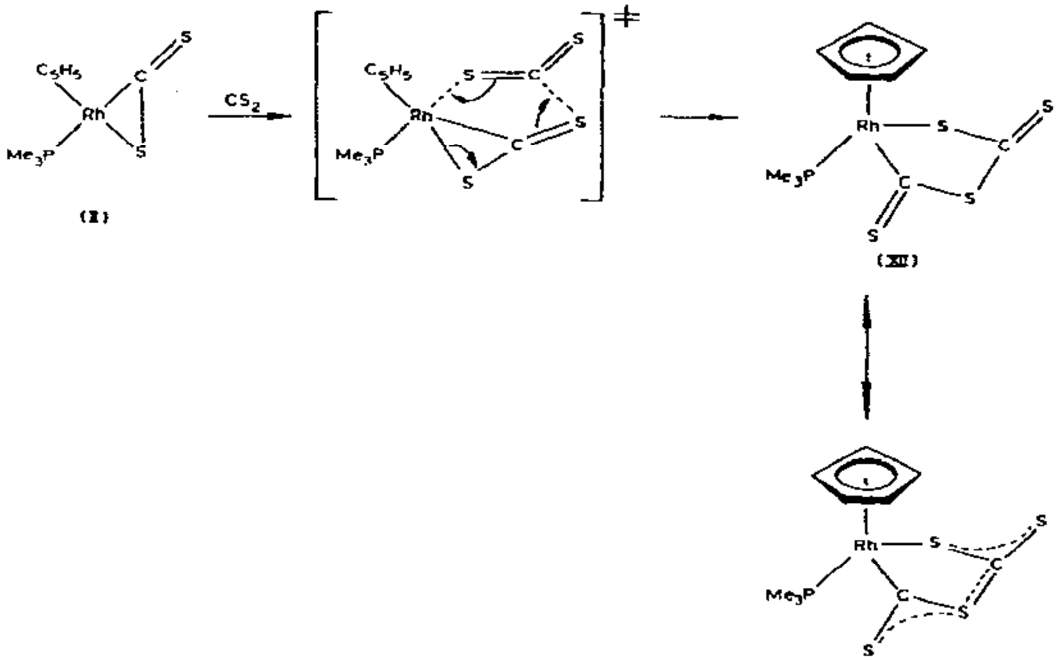
The reaction of (**VII**) with NaH does not lead, however, to $C_5H_5Co(PMe_3)CS$ but to $C_5H_5Co(PMe_3)(\eta^2\text{-}CS_2)$, i.e. elimination of CH_4 instead of MeSH occurs [21]. With other anionic nucleophiles, such as CN^- or SCN^-, the CS_2Me-ligand does not react and thus the neutral compounds (**VIII**) and (**IX**) are obtained. Methylisocyanide and trimethylphosphite react similarly to yield (**X**) and (**XI**) (see Scheme 2). The Co–C σ-bond in the complexes (**VIII**)–(**XI**) appears surprisingly stable, as no cleavage of this bond occurs with weak acids or with excess of L [23].

Scheme 2



In contrast to complex (**I**), the rhodium analogue (**II**) is very labile towards methylating agents and therefore no stable salts of the cation $[C_5H_5Rh(PMe_3)(\eta^2\text{-}CS_2Me)]^+$ could be obtained [23]. The rhodium complex (**II**), however, shows another interesting reaction, namely, the addition of a second CS_2 molecule to form the metalloheterocycle $C_5H_5(PMe_3)RhC_2S_4$ (**XII**) [14]. According to the results of the X-ray analysis, the C_2S_4-fragment is coplanar and possesses nearly identical C–S bond lengths. These C–S bonds are significantly shorter than a C–S single bond which indicates that the chelating C_2S_4-ligand forms a highly delocalized π-electron system [14]. The capability of $(\eta^2\text{-}CS_2)$–metal complexes to behave as a 1,3-dipole and to react with, for example, $C_2(COOMe)_2$ has also been demonstrated by

Wakatsuki [24] and LeBozec et al. [25], who used $C_5H_5Rh(PPh_3)(\eta^2\text{-}CS_2)$ and $Fe(CO)_2[P(OMe)_3]_2(\eta^2\text{-}CS_2)$ as starting materials.

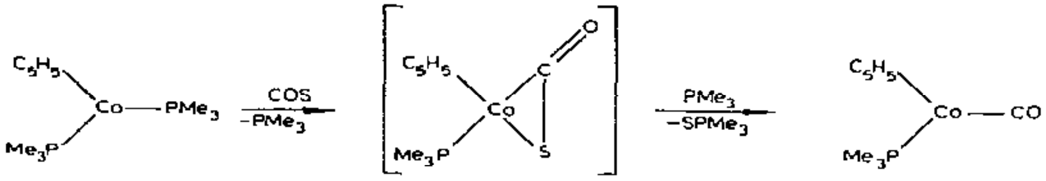


(ii) Complexes obtained from COS and CSSe: a novel route to metal thiocarbonyls

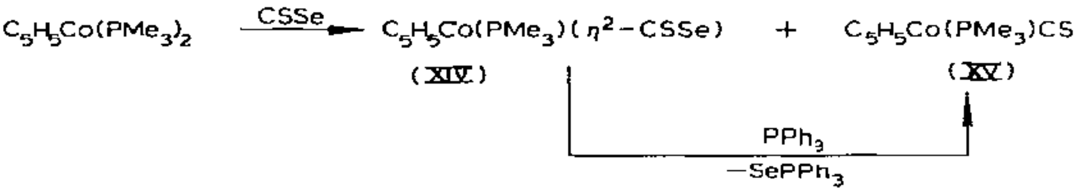
It has already been mentioned that the attempts to prepare the mononuclear thiocarbonyls $C_5H_5M(PMe_3)CS$, particularly with cobalt as metal atom, by sulfur elimination from $C_5H_5M(PMe_3)(\eta^2\text{-}CS_2)$ or by reaction of $[C_5H_5M(PMe_3)(\eta^2\text{-}CS_2Me)]^+$ with hydride ions were unsuccessful. Only the strongly nucleophilic phosphine $P(NMe_2)_3$ reacts with $C_5H_5Co(PMe_3)(\eta^2\text{-}CS_2)$ to form an orange crystalline thiocarbonyl complex $C_5H_5Co[P(NMe_2)_3]CS$ (**XIII**) which is obtained, however, in very low yields [21].

An explanation of the mechanism of the reaction of $C_5H_5Co(PMe_3)_2$ and COS has led to further developments. The only product isolated in practically quantitative yields is the cobalt carbonyl $C_5H_5Co(PMe_3)CO$ which is supposed to be formed via $C_5H_5Co(PMe_3)(\eta^2\text{-}COS)$ as intermediate. The substituted PMe_3 subsequently attacks the coordinated sulfur atom to produce $SPMe_3$ and the carbonyl [26].

Assuming that this proposal is correct and that CSSe behaves analogously to COS, the thiocarbonyl complex $C_5H_5Co(PMe_3)CS$ (**XV**) ought to be



formed from $C_5H_5Co(PMe_3)_2$ and CSSe via the intermediate $C_5H_5Co(PMe_3)(\eta^2\text{-}CSSe)$ (**XIV**). This expectation is at least partially fulfilled. In the reaction of $C_5H_5Co(PMe_3)_2$ with CSSe at −20°C in toluene a mixture of (**XIV**) and (**XV**) is obtained, which can be easily separated due to the difference in solubility of the complexes in hydrocarbons. The thiocarbonylselenide complex (**XIV**) reacts with PPh_3 in benzene to give (**XV**) in quantitative yield [26].



$$C_5H_5Co(PMe_3)_2 \xrightarrow{CSSe} \underset{(\mathbf{XIV})}{C_5H_5Co(PMe_3)(\eta^2\text{-}CSSe)} + \underset{(\mathbf{XV})}{C_5H_5Co(PMe_3)CS}$$

$$(\mathbf{XIV}) \xrightarrow[-SePPh_3]{PPh_3} (\mathbf{XV})$$

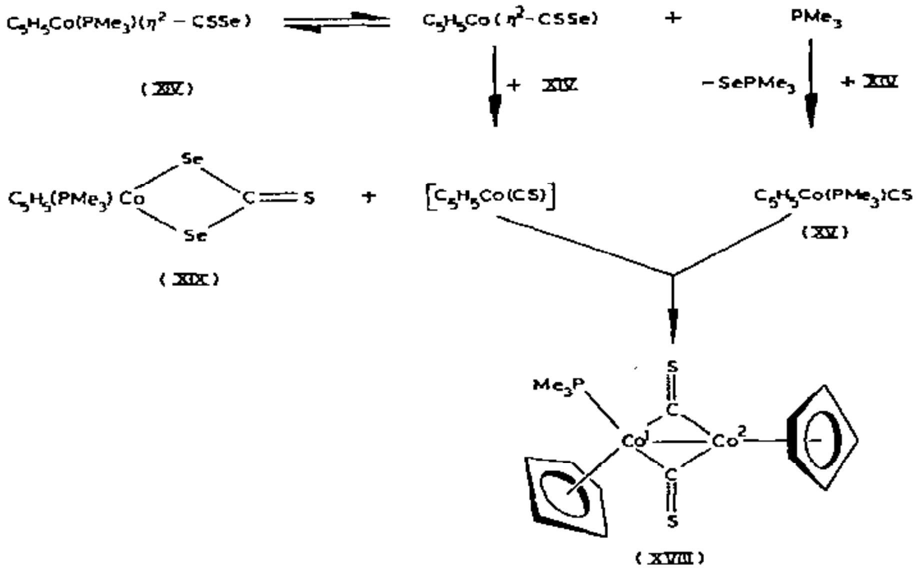
The corresponding rhodium complexes have been similarly prepared [26]. Replacement of the ethylene ligand in $C_5H_5Rh(PMe_3)C_2H_4$ by CSSe leads to $C_5H_5Rh(PMe_3)(\eta^2\text{-}CSSe)$ (**XVI**), which reacts with PPh_3 to yield quantitatively $C_5H_5Rh(PMe_3)CS$ (**XVII**) and $SePPh_3$. Recently, the triphenylphosphine complex $C_5H_5Rh(PPh_3)CS$ has been synthesized from $Rh(PPh_3)_2(CS)Cl$ and NaC_5H_5 [27].

Although it has not yet been possible to obtain single crystals of one of the (η^2-CSSe)-complexes it can be concluded from the clean reactions of (**XIV**) and (**XVI**) with PPh_3, which only yield $C_5H_5M(PMe_3)CS$ and $SePPh_3$, (and *not* $C_5H_5M(PMe_3)CSe$ and $SPPh_3$) that the CSSe ligand is coordinated through the carbon and selenium and not through the carbon and the sulfur atoms. Fenster and Butler [28] have already postulated that the formation of $C_5H_5Mn(CO)_2CS$ from $C_5H_5Mn(CO)_2(\eta^2\text{-}CS_2)$ and PPh_3 proceeds via nucleophilic attack of the phosphine at the sulfur atom bonded to the metal.

During the various attempts to prepare single crystals of (**XIV**), an unexpected reaction of the (η^2-CSSe)-complex has been observed. Dark red crystals precipitated when a toluene solution of (**XIV**) was kept at room temperature for several days. The crystals were shown by X-ray analysis to be the binuclear cobalt complex $C_5H_5(PMe_3)Co(\mu\text{-}CS)_2CoC_5H_5$ (**XVIII**). The NMR spectrum of the solution showed the presence of two other products, $SePMe_3$ and the cobalt diselenothiocarbonate $C_5H_5Co(PMe_3)(Se_2CS)$ (**XIX**), which was independently obtained from $C_5H_5Co(PMe_3)CO$

and CSSe [29]. A possible mechanism for the formation of (**XVIII**) is shown in Scheme 3.

Scheme 3

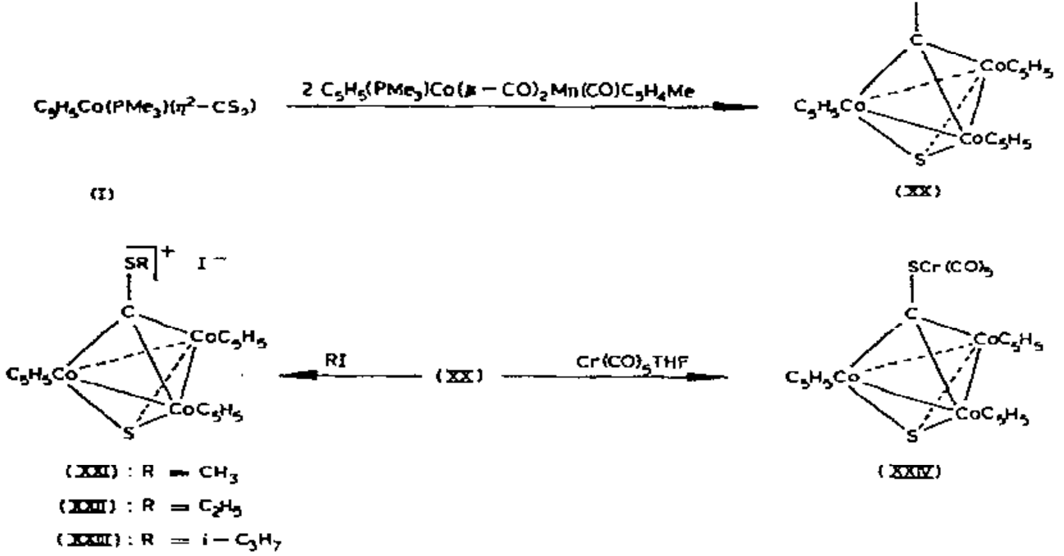


The most notable feature of the structure of the binuclear complex (**XVIII**) is the asymmetry of the thiocarbonyl bridges. The bond-lengths of the μ-CS carbon atoms to the cobalt atom Co^2 are significantly shorter (0.13–0.15 Å) than those to the cobalt atom Co^1, which is linked to the phosphine ligand. The asymmetry can be explained by the tendency of both metal atoms to obtain a closed-shell configuration which is only possible by stronger donation of the CS groups and of the coordinatively saturated cobalt atom Co^1 towards Co^2. The presence of a metal-to-metal bond in (**XVIII**) is indicated by the relatively short Co–Co distance of 2.392 Å [29].

Along with the preparation of the mono- and binuclear cobalt thiocarbonyl compounds (**XV**) and (**XVIII**) we have also successfully synthesized the first trinuclear cobalt complex containing a triply-bridging CS ligand [30]. These studies were not aimed at the preparation of $(C_5H_5Co)_3(S)(CS)$ (**XX**) but rather at the symmetrical dinuclear complex $[C_5H_5(PMe_3)Co]_2(\mu\text{-}CS_2)$ which, according to the work of Herberhold et al. [20], was expected to have a non-rigid structure containing a fluxional CS_2 bridge. Instead of this dinuclear complex the remarkably stable trinuclear cluster (**XX**) (see Scheme 4) was obtained, which was isolated in 82% yield [30].

According to the X-ray structure analysis, the carbon–sulfur bond length in (**XX**) is surprisingly long (1.70 Å) and near to that expected for a C–S single bond [30]. Consequently, the sulfur atom of the μ_3-thiocarbonyl bridge is a highly nucleophilic center. Complex (**XX**), therefore, reacts with alkyl

Scheme 4



iodides, e.g. MeI, EtI and *i*-PrI, to give the salts $[(C_5H_5Co)_3(S)(CSR)]I$ **(XXI)**–**(XXIII)** in which a carbyne unit bridges the three cobalt atoms. The reaction of **(XX)** with $Cr(CO)_5THF$ yields the tetranuclear complex $(C_5H_5Co)_3(S)CSCr(CO)_5$ **(XXIV)**. The X-ray structural analysis of **(XXIV)** shows that the C–S distance in this molecule is nearly the same as in **(XX)** but due to the bending of the CS–$Cr(CO)_5$ moiety to one side, the symmetry of the $Co_3S(CS)$ cluster is reduced [30].

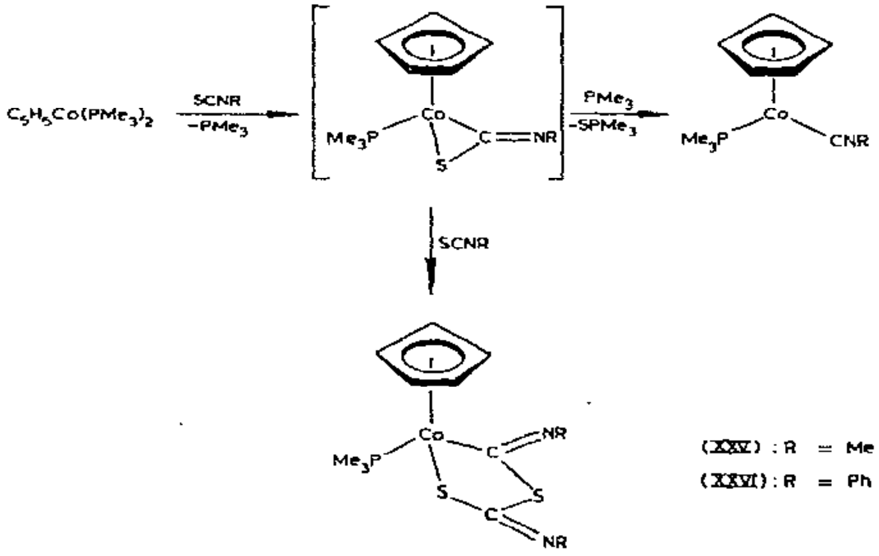
Unexpectedly, the trinuclear complex **(XX)** is also obtained on heating $C_5H_5Co(PMe_3)(\eta^2\text{-}CS_2)$ **(I)** and in the reactions of $C_5H_5Co(PMe_3)(\eta^2\text{-}CS_2)$ with $C_5H_5Rh(PMe_3)C_2H_4$ or of $C_5H_5Rh(PMe_3)(\eta^2\text{-}CS_2)$ **(II)** with $C_5H_5Co(PMe_3)_2$ [30]. In contrast to the strong tendency to form the cobalt cluster **(XX)**, all attempts to produce the analogous rhodium compound $(C_5H_5Rh)_3(S)(CS)$ failed [14]. In the reactions of **(II)** with $C_5H_5Rh(PMe_3)C_2H_4$ or with $C_5H_5(PMe_3)Rh(\mu\text{-}CO)_2Mn(CO)C_5H_4Me$, two possible sources of the coordinatively unsaturated $C_5H_5Rh(PMe_3)$ unit, only mononuclear products, such as $C_5H_5Rh(PMe_3)CS$ **(XVII)** and $C_5H_5Rh(PMe_3)CO$, are formed. Up to now experiments directed to the synthesis of mixed clusters $(C_5H_5Co)_n(C_5H_5Rh)_{3-n}(S)(CS)$ ($n = 1$ or 2) have also remained unsuccessful.

(iii) Complexes obtained from SCNR and OCNR: new metallaheterocycles

The great stability (and inertness towards sulfur abstraction) of $C_5H_5Co(PMe_3)(\eta^2\text{-}CS_2)$ and the supposedly great lability of

$C_5H_5Co(PMe_3)(\eta^2\text{-}COS)$ prompted the question whether the heteroallenes SCNR and OCNR behave like CS_2 or COS in presence of $C_5H_5Co(PMe_3)_2$. For the isothiocyanates the answer is clear: both SCNMe and SCNPh react under mild conditions with the bis(trimethylphosphine)cobalt complex to yield $C_5H_5Co(PMe_3)CNR$ [31]. Therefore, the isothiocyanates behave like COS.

Scheme 5

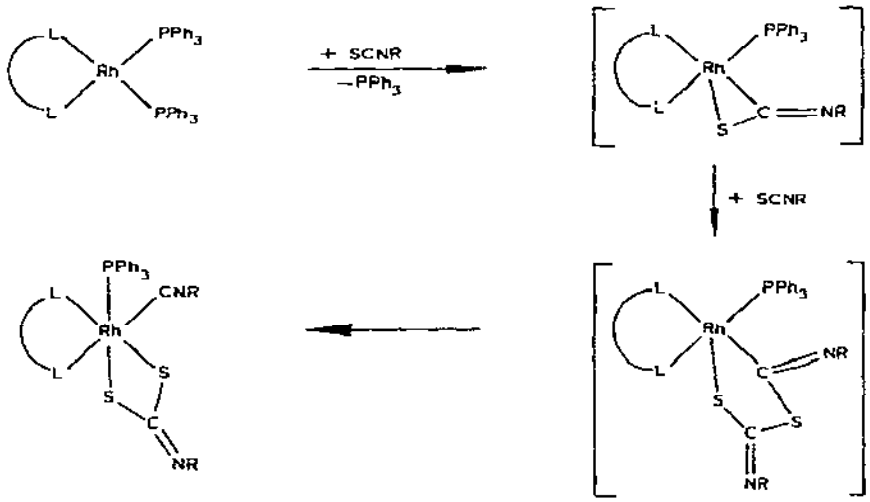


The main reason for postulating that the compounds $C_5H_5Co(PMe_3)(\eta^2\text{-}SCNR)$ are true intermediates in the reactions of $C_5H_5Co(PMe_3)_2$ and SCNR derives from the observation that at somewhat higher temperatures the metallaheterocycles (**XXV**) and (**XXVI**) are formed as by-products (see Scheme 5). These compounds are exceedingly stable and can be easily separated from the isonitrile complexes $C_5H_5Co(PMe_3)CNR$ by their different solubilities in pentane [31].

The formation of structurally related heterocyclic complexes containing rhodium as the central atom has recently been proposed by Thewissen and van Gaal [32], who isolated the dithiocarbonimidato compounds $(L\text{-}L)Rh(PPh_3)(CNR)S_2CNR$ in the reactions of $(L\text{-}L)Rh(PPh_3)_2$ and isothiocyanates. The mechanism shown in Scheme 6 has been postulated.

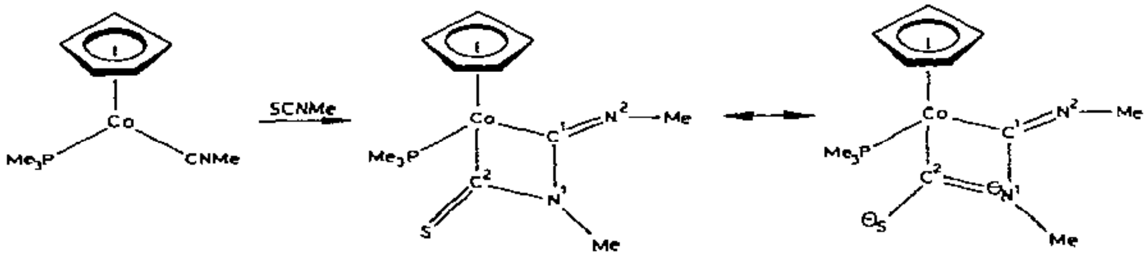
The cobalt carbonyl complex $C_5H_5Co(PMe_3)CO$ which is less nucleophilic than $C_5H_5Co(PMe_3)_2$ [33] also reacts with methylisothiocyanate by displacement of the phosphine ligand to form $C_5H_5Co(CO)CNMe$ and $SPMe_3$ [15]. This contrasts to the behavior of $C_5H_5Co(PMe_3)CO$ toward CS_2 where the CO group is substituted and $C_5H_5Co(PMe_3)(\eta^2\text{-}CS_2)$ (**I**) is formed. Most recently, Fortune and Manning reported that in the reaction of

Scheme 6



$C_5H_5Co(PPh_3)CO$ with SCNPh one of the products is the *dihapto*-bonded phenylisothiocyanate complex $C_5H_5Co(PPh_3)(\eta^2\text{-}SCNPh)$ [34]. It can, therefore, be concluded that the basicity of the complex, which is mainly determined by the type of phosphine coordinated to the metal, plays a dominant role in determining the course of the substitution reaction.

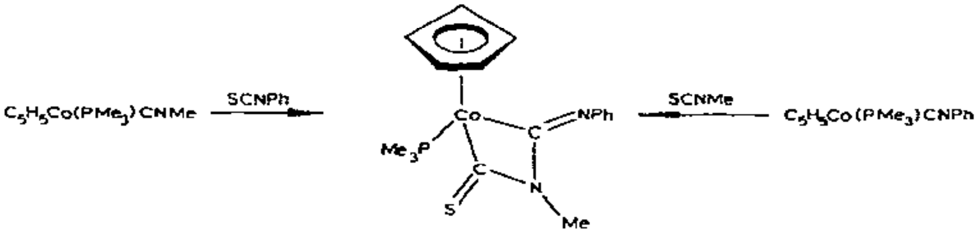
Interestingly, the cobalt methylisonitrile complex $C_5H_5Co(PMe_3)CNMe$ reacts with SCNMe in a manner analogous to $C_5H_5Co(PMe_3)CO$ to form an addition product (**XXVII**) rather than a substitution product [31]. The X-ray structural analysis shows [35] that a cobalt-containing four-membered heterocycle is produced for which the relatively long C–S (1.66 Å) and the relatively short C^2–N^1 (1.35 Å) distances indicate that the following two resonance forms must be considered.



(XXVII)

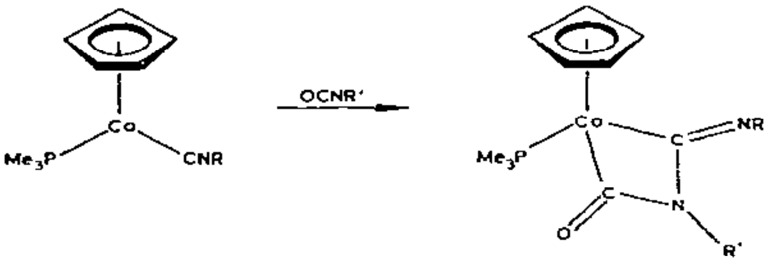
Complex (**XXVII**) is methylated both at the sulfur atom and the nitrogen atom N^2 to yield a dication which has been isolated as the BF_4 salt [35].

The observation that in the reactions of $C_5H_5Co(PMe_3)CNMe$ with SCNPh and of $C_5H_5Co(PMe_3)CNPh$ with SCNMe the same heterocyclic complex (**XXVIII**) is formed deserves particular mention [35]. It has been proved by an X-ray analysis that in (**XXVIII**) again a planar four-membered heterocycle is formed in which the distances between the ring atoms Co, C, N and C are almost identical to those in (**XXVII**).



(XXVIII)

At ambient temperatures, methyl- and phenylisocyanate do not react with $C_5H_5Co(PMe_3)_2$ and thus behave differently from SCNMe and SCNPh. Both isocyanates, however, undergo cycloaddition reactions with $C_5H_5Co(PMe_3)CNR$ leading to the complexes (**XXIX**)–(**XXXI**) [36].

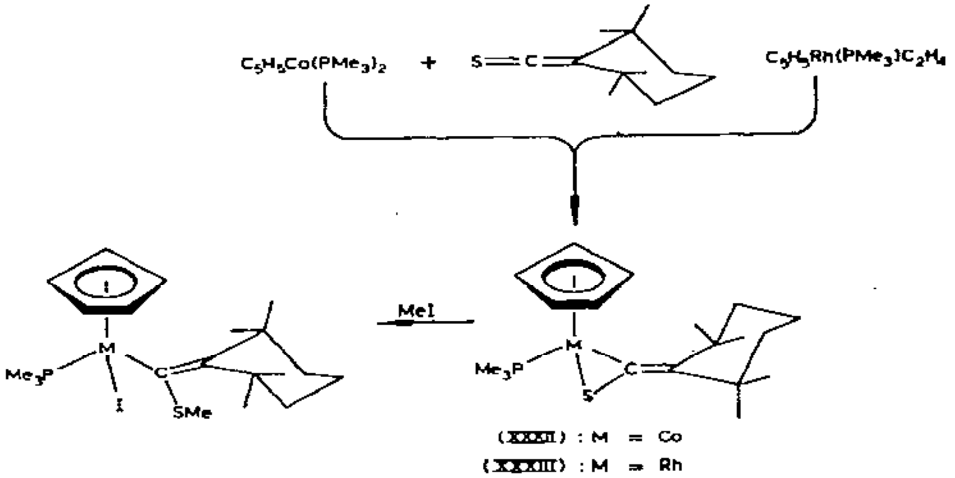


(XXIX) : R = Me, R' = Me
(XXX) : R = Me, R' = Ph
(XXXI) : R = Ph, R' = Me

(iv) Complexes obtained from thioketenes and thioketones

The studies concerned with the reactivity of $C_5H_5M(PMe_3)_2$ and $C_5H_5M(PMe_3)L$ with CS_2 and the related molecules $S=C=E$ ($E=O$, Se and NR) prompted the question whether a similar heteroallene, in which the central carbon atom is linked to a second C atom and thus the bond $C=E$ is less polar, behaves in the same way and also coordinates to the d^8 metal as a *dihapto* ligand. As an accessible substrate 1,1,3,3-tetramethyl-2-thiocarbonylcyclohexane was chosen which, in contrast to other dialkylthioketenes, is remarkably stable. It reacts smoothly with $C_5H_5Co(PMe_3)_2$ as well as with $C_5H_5Rh(PMe_3)C_2H_4$ to give the complexes (**XXXII**) and (**XXXIII**) in nearly quantitative yields [37]. As it is shown in Scheme 7, the reaction of these complexes with MeI lead to cleavage of the M–S bond and addition of the methyl group to the sulfur atom.

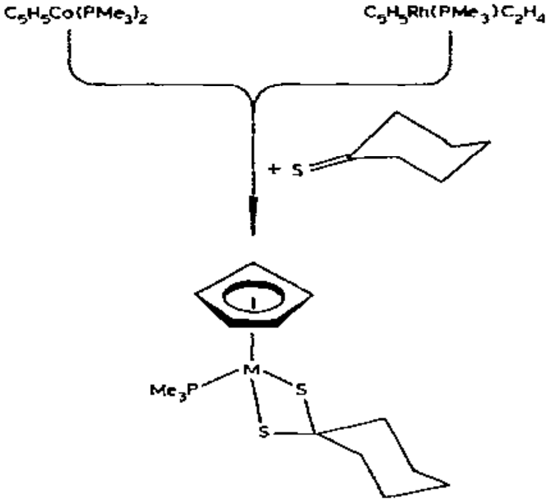
Scheme 7



According to the X-ray structural analysis of (**XXXII**), the coordination of the thioketene is completely analogous to that of CS_2 in complex (**I**), i.e. the Co–C and Co–S distances and also the S–C–S angle in both compounds are nearly identical. The assumption is thus made that thioketenes like CS_2 possess good π-acceptor properties. It should be noted that the same ligand, 1,1,3,3-tetramethyl-2-thiocarbonylcyclohexane (= L), had previously been used by Behrens and coworkers to prepare binuclear complexes containing bridging thioketene ligands, such as $[(\mu\text{-L})Fe(CO)_3]_2$ and $[(\mu\text{-L})CoC_5H_5]_2$, and mononuclear complexes such as $LCr(CO)_5$ in which the heteroallene presumably is only coordinated via the sulfur atom [38].

Thiocyclohexanone, a thioketone which is structurally related to the above-mentioned thioketene L, also reacts with $C_5H_5Co(PMe_3)_2$ and $C_5H_5Rh(PMe_3)C_2H_4$ to yield products (**XXXIV**) and (**XXXV**) in which the dianionic chelating ligand $S_2CC_5H_{10}^{2-}$ is bonded to the metal [23]. The formation of this new ligand resembles that of the diselenothiocarbonate in the reaction of $C_5H_5Co(PMe_3)CO$ and CSSe. It is not yet known whether the synthesis of the chelate complexes (**XXXIV**) and (**XXXV**) proceeds via the intermediate $C_5H_5M(PMe_3)(\eta^2\text{-}SCC_5H_{10})$ or whether the dianionic ligand is primarily formed in a metal-promoted disproportionation reaction.

Scheme 8



(XXXIV) : = Co
(XXXV) : = Rh

C. PALLADIUM COMPLEXES

The phosphine palladium complexes $Pd(PR_3)_n$ were selected as starting materials for the reasons already discussed in the introduction of this review article. There is some evidence [39] that these palladium complexes are more nucleophilic than their nickel and platinum analogues and, therefore, it is not surprising that they readily react with CS_2 and other heteroallenes. The surprising fact is, however, that in most of the reactions which have been studied up to now the types of the products which are formed, for example, from $C_5H_5Co(PMe_3)_2$ or $C_5H_5Rh(PMe_3)C_2H_4$ and CS_2, CSSe, COS, SCNR, etc. and from $Pd(PR_3)_n$ and the same heteroallenes, are different.

(i) Complexes obtained from CS_2 and CSSe: the expected and the unexpected products

The triphenylphosphine complex $Pd(PPh_3)_4$, already used by Baird and Wilkinson [3], reacts with CS_2 to give the well-characterized product $Pd(PPh_3)_2(\eta^2\text{-}CS_2)$ [40] which does not react with excess PPh_3 to yield the corresponding palladium thiocarbonyl. This behavior is similar to that of the cobalt and rhodium complexes $C_5H_5M(PMe_3)(\eta^2\text{-}CS_2)$, which are also inert towards PPh_3.

As the *dihapto*-bonded thiocarbonylselenide ligand in $C_5H_5M(PMe_3)(\eta^2\text{-}$

CSSe) is readily transformed on reaction with PPh_3 into the thiocarbonyl group [26], we expected the same reaction pattern for the palladium complexes $Pd(PR_3)_2(\eta^2\text{-}CSSe)$. The experiments designed to test this hypothesis led to the first unexpected result. Whereas $Pd(PPh_3)_4$ reacts with CSSe to form $Pd(PPh_3)_2(\eta^2\text{-}CSSe)$ (**XXXVIII**), other analogous phosphine palladium complexes $Pd(PR_3)_4$ (where PR_3 is $PMePh_2$, PMe_2Ph and PMe_3) yield binuclear products of general composition $[(PR_3)Pd(SeSCPR_3)]_2$ (**XL**), (**XLII**), (**XLIV**) [41].

The same difference in behavior is also observed in the corresponding reactions of $Pd(PR_3)_4$ with CS_2. Only the methyldiphenylphosphine complex behaves like the PPh_3 analogue and forms the expected ($\eta^2\text{-}CS_2$)-compound (**XXXIX**). The other phosphine complexes surprisingly react with CS_2 to form the binuclear products $[(PR_3)Pd(S_2CPR_3)]_2$ (**XLI**), (**XLIII**) [41]. In contrast to $Pd(PMe_3)_4$, the triisopropylphosphinepalladium compounds $Pd(PPr^i_3)_3$ and $Pd(PPr^i_3)_2$ react with CS_2 and CSSe to form the mononuclear complexes $Pd(PPr^i_3)_2(\eta^2\text{-}CS_2)$ (**XXXVI**) and $Pd(PPr^i_3)_2(\eta^2\text{-}CSSe)$ (**XXXVII**).

Complex **XLIII** with $PR_3 = PMe_3$ is also obtained from $Pd(PPh_3)_2(\eta^2\text{-}CS_2)$, $Pd(PMePh_2)_2(\eta^2\text{-}CS_2)$ or $Pd(PPr^i_3)_2(\eta^2\text{-}CS_2)$ and PMe_3 or from $Pd(PMe_3)_4$ and the zwitter-ion PMe_3CS_2. Furthermore by using PMe_3CS_2 and PMe_2PhCS_2 it is possible to synthesize the "mixed" binuclear compounds (**XLV**)–(**L**) in which the phosphine groups coordinated to the metal and to the carbon atom of the zwitter-ion are different. The complex (**XLIII**) slowly reacts with excess of trimethylphosphine to yield the mononuclear compound $[Pd(PMe_3)_2(S_2CPMe_3)]$ (**LI**) [41].

The results presently available are summarized in the following equations.

$$Pd(PR_3)_n + CSE \rightarrow Pd(PR_3)_2(\eta^2\text{-}CSE) + (n-2)PR_3$$

(XXXVI): $PR_3 = PPr^i_3$; $E = S$
(XXXVII): $PR_3 = PPr^i_3$; $E = Se$
(XXXVIII): $PR_3 = PPh_3$; $E = Se$
(XXXIX): $PR_3 = PMePh_2$; $E = S$

$$2\ Pd(PR_3)_4 + 2\ CSE \rightarrow [(PR_3)Pd(ESCPR_3)]_2 + 4\ PR_3$$

(XL): $PR_3 = PMePh_2$; $E = Se$
(XLI): $PR_3 = PMe_2Ph$; $E = S$
(XLII): $PR_3 = PMe_2Ph$; $E = Se$
(XLIII): $PR_3 = PMe_3$; $E = S$
(XLIV): $PR_3 = PMe_3$; $E = Se$

$$2\ Pd(PR_3)_2(\eta^2\text{-}CS_2) + 4\ PMe_3 \rightarrow \underset{\textbf{(XLIII)}}{[(PMe_3)Pd(S_2CPMe_3)]_2} + 4\ PR_3$$

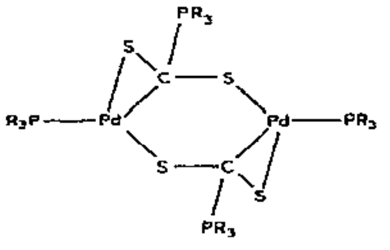
$(PR_3 = PPr^i_3,\ PPh_3,\ PMePh_2)$

$$2\,Pd(PR_3)_n + 2\,PR'_3CS_2 \rightarrow [(PR_3)Pd(S_2CPR'_3)]_2 + 2(n-1)PR_3$$

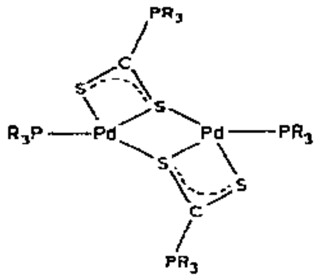
(XLV): $PR_3 = PPr^i_3$; $PR'_3 = PMe_3$
(XLVI): $PR_3 = PPh_3$; $PR'_3 = PMe_3$
(XLVII): $PR_3 = PMePh_2$ $PR'_3 = PMe_3$
(XLVIII): $PR_3 = PMe_2Ph$ $PR'_3 = PMe_3$
(XLIII): $PR_3 = PMe_3$; $PR'_3 = PMe_3$
(XLIX): $PR_3 = PPh_3$; $PR'_3 = PMe_2Ph$
(L): $PR_3 = PMePh_2$; $PR'_3 = PMe_2Ph$
(XLI): $PR_3 = PMe_2Ph$; $PR'_3 = PMe_2Ph$

(LI)

The crucial problem in this context is of course the structure of the binuclear complexes. Despite numerous attempts failure to isolate single crystals resulted, mainly due to the lability of the complexes in solution. There is no doubt from the methods of synthesis and the reactivity that in each compound two phosphine ligands and two zwitter-ions are present, the latter probably bridging two metal atoms. It has also been shown that the complexes are chiral. In the ^{1}H-NMR spectra of, for example, **(XLI)**, **(XLV)** and **(L)** two signals for the enantiotopic $PCH(CH_3)_2$ and $P(CH_3)_2$ methyl groups are observed [41]. For the compounds containing the PR_3CS_2 zwitter-ions as ligands, the two following proposals may fit with the analytical and spectroscopic results.

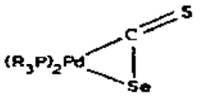


(A)

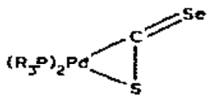


(B)

The structure of the complexes obtained from CSSe is also still an unresolved problem. From the infrared data, it seems possible that in the mononuclear compounds **(XXXVII)** and **(XXXVIII)** both isomeric forms are

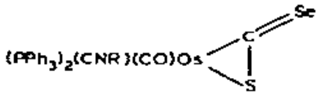


and



present [41]. Most recently Roper and co-workers [42] succeeded in preparing by two different routes the corresponding isomers (**LII**) and (**LIII**), which are configurationally stable in solution.

(LII)



(LIII)

The binuclear complexes (**XL**), (**XLII**) and (**XLIV**) probably have a similar structure to that of the compounds containing the PR_3CS_2 groups as ligands although it cannot be decided whether the sulfur or the selenium atoms of the zwitterions PR_3CSSe are in the bridging positions.

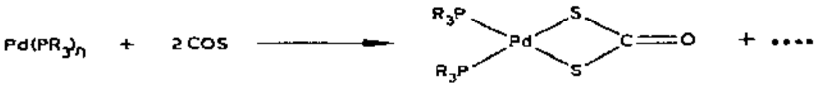
It is interesting to note that the formation of the zwitterionic ligand PMe_3CS_2 during insertion of CS_2 into a Pd–PMe_3 bond is not restricted to palladium(0). We have found that both the neutral and the cationic trimethylphosphine palladium(II) complexes, *trans*-[$(PMe_3)_2Pd(COMe)I$] and [$(PMe_3)_3PdR$]$^+$ (R = Me, Ph, COMe), react with CS_2 to yield the products [$(PMe_3)(PMe_3CS_2)Pd(COMe)I$] and [$(PMe_3)_2Pd(S_2CPMe_3)R$]$^+$, respectively [43]. In the reaction of [$(PMe_3)_3PdH$]$^+$ with CS_2 the cation [$(PMe_3)_2Pd(S_2CHPMe_3)$]$^+$ is formed, presumably via primary insertion of CS_2 into the Pd–PMe_3 bond *trans* to the hydride and subsequent migration of the hydride ligand to the carbon atom of the zwitterion [43].

(ii) Complexes obtained from COS and SCNR

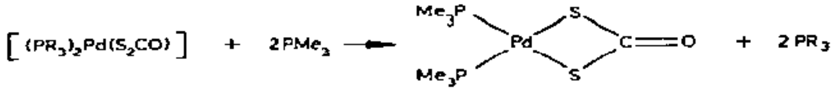
In contrast to $C_5H_5Co(PMe_3)_2$, the phosphine palladium complexes $Pd(PR_3)_n$ do not react with carbonylsulfide and isothiocyanates to form CO or CNR containing products. Whereas $Pd(PPh_3)_4$ is rather inert towards COS, the corresponding compounds $Pd(PMePh_2)_4$, $Pd(PMe_2Ph)_4$ and $Pd(PPr^i_3)_n$ ($n = 2$ or 3) readily react with COS to give the dithiocarbonates [$(PR_3)_2Pd(S_2CO)$] (**LIV**)–(**LVI**) in high yields [44]. The trimethylphosphine complex [$(PMe_3)_2Pd(S_2CO)$] (**LVII**) which is not accessible from $Pd(PMe_3)_4$ and COS, is quantitatively obtained by phosphine exchange with PMe_3 in **LIV**, **LV** or **LVI**.

The dimethylphenylphosphine complex (**LV**) has been characterized by an X-ray structural analysis [44]. Whereas the Pd–S bond lengths in (**LV**) and $Pd(PPh_3)_2(\eta^2\text{-}CS_2)$ are nearly identical, the S–C distances in both compounds are significantly different; in (**LV**) they nearly correspond to that of a S–C single bond. The coordination of the palladium in the dithiocarbonate palladium(II) complex is not strictly planar, the angle between the PPdP and the SPdS planes being 8.4°.

The mechanism of formation of the dithiocarbonate ligand in the reac-



(LIV) : PR$_3$ = PMePh$_2$
(LV) : PR$_3$ = PMe$_2$Ph
(LVI) : PR$_3$ = PPr$^i_3$

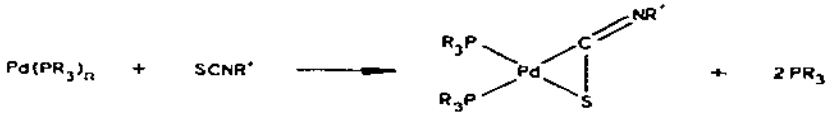


(LIV)-(LVI)

(LVII)

tions of Pd(PR$_3$)$_n$ and COS is not yet clear. The most reasonable assumption is that primarily a Pd(η^2-CSO) and then either a Pd(η^2-CSO)(η^1-CSO) or a heterocyclic $\overline{\mathrm{PdSC(O)SC}}$(O) intermediate is formed which eliminates CO to yield the product. The primary formation of Pd(PR$_3$)$_2$(η^2-CSO) would be analogous to the observation that the corresponding platinum complex Pt(PPh$_3$)$_2$(η^2-COS), already prepared by Baird and Wilkinson [3], reacts with COS to give the dithiocarbonate [(PPh$_3$)$_2$Pt(S$_2$CO)] [44], which erroneously had been described as a bis(carbonylsulfide) compound Pt(PPh$_3$)$_2$(COS)$_2$ [45]. The same complex [(PPh$_3$)$_2$Pt(S$_2$CO)] is produced in the reactions of Pt(PPh$_3$)$_2$(O$_2$) or Pt(PPh$_3$)$_2$(SO$_2$) with CS$_2$ and of Pt(PPh$_3$)$_2$(η^2-CS$_2$) with SO$_2$ [46,47]. It should be mentioned that there are several examples known in the literature proving that CO$_3^{2-}$ and CS$_3^{2-}$ ligands are formed in reactions of metal compounds with CO$_2$ and CS$_2$, respectively [48].

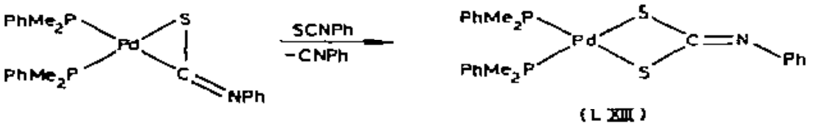
In the reactions of the phosphine palladium complexes Pd(PR$_3$)$_n$ with isothiocyanates, the mechanism is rather obvious. The compounds where PR$_3$ is PMe$_3$, PMe$_2$Ph, PMePh$_2$ and PPr$^i_3$ react with SCNR′ in hexane to form the expected mononuclear products Pd(PR$_3$)$_2$(η^2-SCNR′) in which it is assumed that a *dihapto*-coordination of the isothiocyanate ligand via the carbon and sulfur atom occurs in a manner similar to the coordination of carbondisulfide in Pd(PR$_3$)$_2$(η^2-CS$_2$) [49].



(LVIII): PR$_3$ = PMe$_3$; R′ = Ph
(LIX) : PR$_3$ = PMe$_2$Ph ; R′ = Ph
(LX) : PR$_3$ = PMePh$_2$; R′ = Ph
(LXI) : PR$_3$ = PPr$^i_3$; R′ = Ph
(LXII) : PR$_3$ = PMe$_2$Ph ; R′ = Me

The same bonding mode has been suggested by Itoh et al. for the bis(triphenylphosphine) complexes $Pd(PPh_3)_2(\eta^2\text{-}SCNR)$ where R is COPh, COC_6H_4-*p*-Me, COOEt or $CONMe_2$ [50].

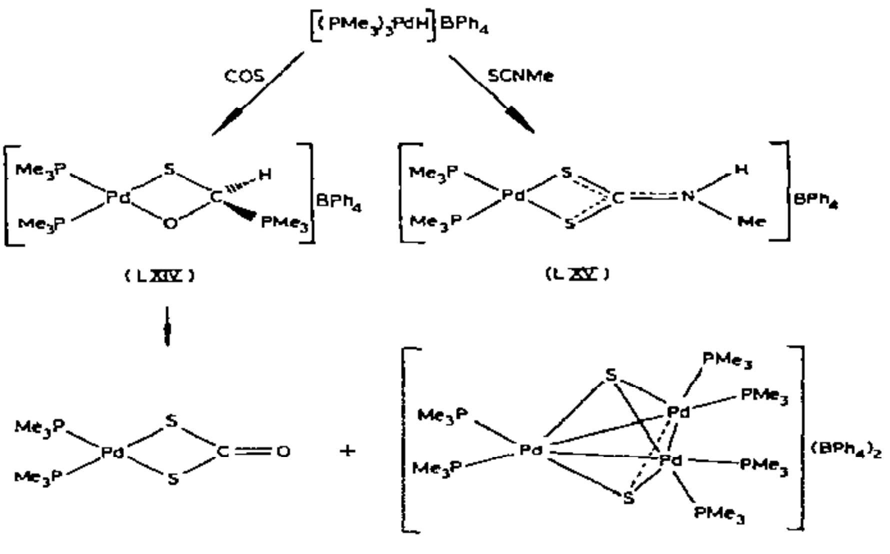
Complex (**LIX**) reacts with a second molecule of phenylisothiocyanate to form $[(PMe_2Ph)_2Pd(S_2CNPh)]$ (**LXIII**) [49]. The same product is obtained when $Pd(PMe_2Ph)_4$ is treated not with an equivalent amount but with an excess of SCNPh. The course of the reaction of this palladium(0) complex $Pd(PMe_2Ph)_4$ with SCNPh thus resembles that of the reactions of the rhodium(I) compound $Rh(PPh_3)_3Cl$ with various isothiocyanates SCNR ($R = Et, Bu^n, Bu^t$, Ph, CH_2Ph, C_6H_{11}) where only products containing the corresponding dithiocarbonimidato ligand S_2CNR^{2-} are obtained [51].



(LXIII)

Finally, it should be mentioned that COS and SCNMe also react with the hydrido palladium(II) cation $[(PMe_3)_3PdH]^+$ to form an insertion product. Whereas in the reaction with COS, the primary product (**LXIV**) presumably has an analogous structure to that of $[(PMe_3)_2Pd(S_2CHPMe_3)]BPh_4$ (formed from $[(PMe_3)_3PdH]BPh_4$ and CS_2) the product obtained from SCNMe is the dithiocarbamate complex $[(PMe_3)_2Pd(S_2CNHMe)]BPh_4$ (**LXV**).

Scheme 9



(LXIV)

(LXV)

(LVII)

(LXVI)

On standing in solution, compound (**LXIV**) forms the palladium dithiocarbonate (**LVII**) and, although in low yields, the trinuclear complex $[(PMe_3)_6Pd_3(\mu_3\text{-}S)_2](BPh_4)_2$ (**LXVI**). In (**LXVI**) the X-ray structural analysis shows that the palladium and the sulfur atoms form a slightly distorted trigonal bipyramid [52]. The same complex can be more conveniently prepared from $[Pd(CH_3CN)_4](BF_4)_2$, H_2S and PMe_3 in presence of $NaBPh_4$, a method already used by Sacconi and co-workers to obtain the corresponding nickel compound $[(PEt_3)_6Ni_3(\mu_3\text{-}S)_2](BPh_4)_2$ [53].

ACKNOWLEDGEMENTS

It is a great pleasure for me to acknowledge the contribution of my coworkers cited in the references, in particular Dr. K. Leonhard, Dr. S. Lotz, Dr. B. Juthani, Dr. W. Bertleff, B. Heiser and O. Kolb. I would also like to thank Dr. U. Schubert of the Technical University of Munich and Dr. Ch. Burschka of this institute for determining the crystal structure of some of our complexes. The continuing financial support of the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is greatly acknowledged.

REFERENCES

1 M.C. Baird and G. Wilkinson, Chem. Commun., (1966) 514.
2 R. Mason and A.I.M. Rae, J. Chem. Soc. A, (1970) 1767.
3 M.C. Baird and G. Wilkinson, J. Chem. Soc. A, (1967) 865.
4 M.C. Baird and G. Wilkinson, Chem. Commun., (1966) 267.
5 I.S. Butler and A.E. Fenster, J. Organomet. Chem., 66 (1974) 161.
6 P.V. Yaneff, Coord. Chem. Rev., 23 (1977) 183.
7 F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 4th edn., Wiley, New York, 1980, Chapt. 29.
8 H. Werner, Angew. Chem., 89 (1977) 1; Angew. Chem. Int. Ed. Engl., 16 (1977) 1.
9 H. Werner, H. Neukomm and W. Kläui, Helv. Chim. Acta, 60 (1977) 326; H. Neukomm and H. Werner, J. Organomet. Chem., 108 (1976) C26.
10 H. Werner and W. Hofmann, Chem. Ber., 110 (1977) 3481.
11 H. Werner, R. Feser and W. Buchner, Chem. Ber., 112 (1979) 834.
12 H. Werner and W. Bertleff, J. Chem. Res. (M), (1978) 2720; (S), (1978) 201.
13 H. Werner, K. Leonhard and Ch. Burschka, J. Organomet. Chem., 160 (1978) 291.
14 H. Werner, O. Kolb, R. Feser and U. Schubert, J. Organomet. Chem., 191 (1980) 283.
15 H. Werner and B. Juthani, J. Organomet. Chem., 209 (1981) 211.
16 K. Leonhard and H. Werner, Angew. Chem., 89 (1977) 656; Angew. Chem. Int. Ed. Engl., 16 (1977) 649.
17 Y. Wakatsuki and H. Yamazaki, J. Organomet. Chem., 64 (1974) 393.
18 M. Herberhold and M. Süss-Fink, Angew. Chem., 89 (1977) 192; Angew. Chem. Int. Ed. Engl., 16 (1977) 194.
19 P.J. Vergamini and P.G. Eller, Inorg. Chim. Acta, 34 (1979) L291.
20 M. Herberhold, M. Süss-Fink and C.G. Kreiter, Angew. Chem., 89 (1977) 191; Angew. Chem. Int. Ed. Engl., 16 (1977) 193.

21 O. Kolb, Diploma Thesis, University of Würzburg, 1979.
22 T.J. Collins, W.R. Roper and K.G. Town, J. Organomet. Chem., 121 (1976) C41.
23 H. Werner and O. Kolb, unpublished results, 1980.
24 Y. Wakatsuki, H. Yamazaki and H. Iwasaki, J. Am. Chem. Soc., 95 (1973) 5781.
25 H. LeBozec, A. Gorgues and P. Dixneuf, J. Am. Chem. Soc., 100 (1978) 3946.
26 H. Werner and O. Kolb, Angew. Chem., 91 (1979) 930; Angew. Chem. Int. Ed. Engl., 18 (1979) 865.
27 F. Faraone, G. Tresoldi and G.A. Loprete, J. Chem. Soc., Dalton Trans., (1979) 933.
28 A.E. Fenster and I.S. Butler, Inorg. Chem., 13 (1974) 915.
29 H. Werner, O. Kolb, U. Schubert and K. Ackermann, Chem. Ber., in press.
30 H. Werner and K. Leonhard, Angew. Chem., 91 (1979) 663; Angew. Chem. Int. Ed. Engl., 18 (1979) 627; H. Werner, K. Leonhard, O. Kolb, E. Röttinger and H. Vahrenkamp, Chem. Ber., 113 (1980) 1654.
31 H. Werner, S. Lotz and B. Heiser, J. Organomet. Chem., 209 (1981) 197.
32 D.H.M.W. Thewissen and H.L.M. van Gaal, J. Organomet. Chem., 171 (1979) 69.
33 A. Spencer and H. Werner, J. Organomet. Chem., 171 (1979) 219.
34 J. Fortune and A.R. Manning, J. Organomet. Chem., 190 (1980) C95.
35 H. Werner, B. Heiser and Ch. Burschka, Chem. Ber., in press.
36 B. Heiser and H. Werner, unpublished results.
37 H. Werner, O. Kolb, U. Schubert and K. Ackermann, Angew. Chem., 93 (1981) 583; Angew. Chem. Int. Ed. Engl., 20 (1981) 593.
38 U. Behrens and F. Edelmann, J. Organomet. Chem., 118 (1976) C41; D. Wormsbächer, F. Edelman and U. Behrens, Chem. Ber., 114 (1981) 153; U. Behrens, private communication.
39 J.K. Stille and K.S.Y. Lau, Acc. Chem. Res., 10 (1977) 434.
40 T. Kashiwagi, N. Yasuoka, T. Ueki, N. Kasai, M. Kakudo, S. Takahashi and N. Hagihara, Bull. Chem. Soc. Jpn., 41 (1968) 296.
41 W. Bertleff and H. Werner, Chem. Ber., in press; see: W. Bertleff, Ph.D. Thesis, University of Würzburg, 1981.
42 P.J. Brothers, C.E.L. Headford and W.R. Roper, J. Organomet. Chem., 195 (1980) C29.
43 H. Werner and W. Bertleff, Chem. Ber., 113 (1980) 267.
44 H. Werner, W. Bertleff, B. Zimmer-Gasser and U. Schubert, Chem. Ber., in press.
45 R.K. Poddar and U. Agarwala, J. Coord. Chem., 6 (1977) 207.
46 P.J. Hayward, D.M. Blake, G. Wilkinson and C.J. Nyman, J. Am. Chem. Soc., 92 (1970) 5873.
47 J. Ghatak, D.M.P. Mingos, M.B. Hursthouse and P.R. Raithby, Trans. Metal. Chem., 1 (1976) 119.
48 J. Chatt, M. Kubota, G.J. Leigh, F.C. March, R. Mason and D.J. Yarrow, Chem. Commun., (1974) 1033; I.B. Benson, J. Hunt, S.A.R. Knox and V. Oliphant, J. Chem. Soc. Dalton Trans., (1978) 1240; G. Fachinetti, C. Floriani, A. Chiesi-Villa and C. Guastini, J. Am. Chem. Soc., 101 (1979) 1767; D.H.M.W. Thewissen, J. Organomet. Chem., 188 (1980) 211.
49 W. Bertleff and H. Werner, Chem. Ber., in press.
50 K. Itoh, I. Matsuda, F. Ueda, Y. Ishii and J.A. Ibers, J. Am. Chem. Soc., 99 (1977) 2118.
51 R.O. Harris, J. Powell, A. Walker and P.V. Yaneff, J. Organomet. Chem., 141 (1977) 217.
52 H. Werner, W. Bertleff and U. Schubert, Inorg. Chim. Acta, 43 (1980) 199.
53 C.A. Ghilardi, S. Midollini and L. Sacconi, Inorg. Chim. Acta, 31 (1978) L431.