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ISOCYANIDE AND HETEROALLENE BRIDGED METAL COMPLEXES

VI *. REACTIONS OF CARBON DISULFIDE IRON, PALLADIUM AND PLATINUM COMPLEXES WITH ELECTROPHILES. EVIDENCE FOR A η^2-CS_2H LIGAND

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Summary

S-Alkylation of $[M(\eta^2\text{-}CS_2)(PPh_3)]_2$ (M = Pd, Pt) is achieved using stoichiometric amounts of the 'hard' alkylating agents $[Et_3O][BF_4]$ and CF_3SO_2OMe, while MeI or 1,2-diiodoethane give $[(Ph_3P)_2(I)Pt(\mu\text{-}CS_2)Pt(PPh_3)_2]I$ and $[(Ph_3P)_2(I)Pt(\mu\text{-}CS_2)Pt(I)PPh_3]$, respectively. Protonation of $[Fe(\eta^2\text{-}CS_2)(CO)_2L_2]$ (L = PMe_2Ph, PPh_3) affords extremely labile complexes containing the novel η^2-CS_2H ligand. The first cationic $\eta^2:\eta^1$-CS_2 bridged dinuclear complexes $[L_2(OC)_2Fe(SCS)Pt(Cl)(PPh_3)_2][BF_4]$ (L = PMe_2Ph, PPh_3) serve as models for the assumed intermediate in the formation of metallodithiocarboxylato(*S*,*S'*) metal compounds.

The great interest in heteroallene activation by transition metals centres to a remarkable extent upon Wilkinson's CS_2 complexes $[Fe(\eta^2\text{-}CS_2)(CO)_2(PR_3)_2]$ and $[M(\eta^2\text{-}CS_2)(PPh_3)_2]$ (M = Pd, Pt) [1]. Though known since 1967, their substitution [2–6], alkylation [6-8], sulfur abstraction [9] and acetylene addition reactions [10–12] have been studied only in recent years, as has the ability of the compounds to act as mono- or bi-dentate ligands via utilization of one or both sulfur atoms [13–15]. There are, however, more differences than similarities in the reactivities of the η^2-CS_2 moiety in the iron and platinum compounds. Thus, while $[Fe(\eta^2\text{-}CS_2)(CO)_2(PR_3)_2]$ readily forms dithiocarbene complexes with alkynes, which among other products afford tetrathiafulvalenes upon decomposition in air [12], $[Pt(\eta^2\text{-}CS_2)(PPh_3)_2]$ does

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* For the previous paper in this series see ref. 32.

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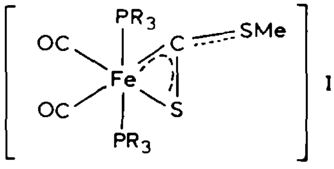
not give a clear-cut reaction with dimethylacetylene dicarboxylate [16]. There are also considerable differences between the ease of CS_2 desulfurization [9,16] and alkylation (vide infra) in these complexes.

To further elucidate the variations in reactivity of CS_2 bound to different metals in an η^2-fashion, we have now carried out comparative studies of the electrophilic reactions on the above mentioned compounds, including protonation, which gives rise to the hitherto unknown η^2-CS_2H ligand.

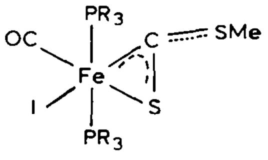
Results and discussion

1. Alkylation studies

Neat methyl iodide transforms CS_2 in (η^2-carbon disulfide)bis(triphenylphosphine)platinum into a dialkylated η^1-dithiocarbene ligand which has been isolated as both the cationic $[Pt(I)(C(SMe)_2)(PPh_3)_2]I$ and the neutral $[PtI_2\{C(SMe)_2\}PPh_3]$ [8]. In contrast, $[Fe(\eta^2\text{-}CS_2)(CO)_2(PR_3)_2]$ under the same conditions goes only to the monoalkylated salt-like species **1** or its neutral counterpart **2** [7].



(1)



(2)

For the preparation of analogous platinum compounds, a strictly stoichiometric alkylation of $[Pt(\eta^2\text{-}CS_2)(PPh_3)_2]$ seemed advisable. With MeI, however, a rather unexpected result was obtained; the reaction in benzene proceeded with a change of colour to give an air-stable yellow solid (**3a**) (eq. 1) which, according to the proton NMR, did not contain a methyl group. Its IR band pattern in the 850–950 cm^{-1} region is consistent with its belonging to the class of metallodithiocarboxylato(S,S′) metal complexes.

This type of μ_2-CS_2 bridge bonding has been extensively studied in our group, and was found to exhibit very characteristically two bands in the IR spectrum with a separation of only 55 cm^{-1} (Table 1) [14,15]. It appears, that platiniodithiocarboxylato(*S*, *S′*)platinum type complexes be at particularly low minima on the potential energy surface. For their generation, which requires halide transfer to the carbene carrying platinum atom, almost any halogen source is effective. This is confirmed by the reaction of $[Pt(\eta^2\text{-}CS_2)(PPh_3)_2]$ with 1,2-diiodoethane to give the related product (**3b**) (eq. 1).

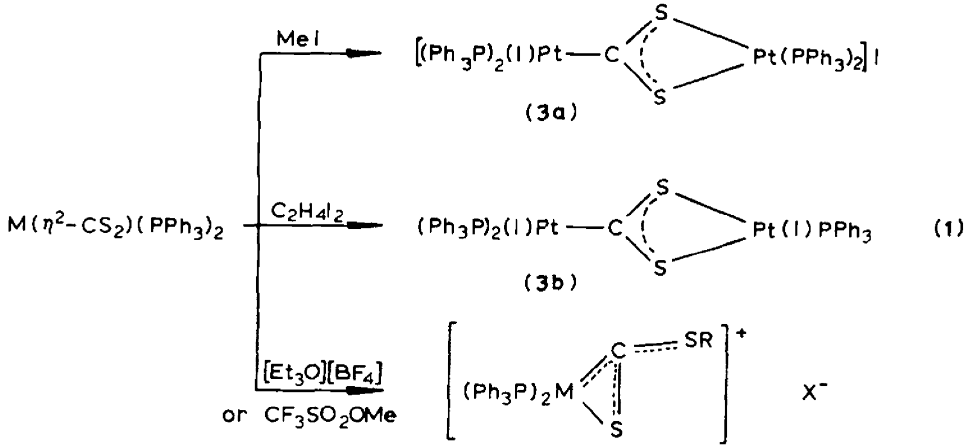
Alkylating agents with non-coordinating anions, on the other hand, produce the desired platinum group analogues of the well-established η^2-CS_2R iron (**1**), osmium, vanadium and tungsten complexes [17–19]. Though rather labile, these orange (**4**) to yellow (**5**) products have been characterized by elementary analysis, IR and ^1H NMR spectra (cf. Tables 1, 3). Depending on the drying conditions, up to one molecule of ether per formula unit is retained in the microcrystalline material. Practically unshifted $\nu(CS)$-absorptions indicate that the CS_2 moiety in the starting complexes ($\nu(CS)$: 1178, 636 (Pd); 1144, 652 (Pt) cm^{-1}) is little perturbed by the addition of R^+. On treatment with tetraethylammonium iodide, **5a** is converted into **3b**.

TABLE 1

SELECTED IR (cm^{-1}) AND ^1H NMR DATA (ppm)

	$\nu(CS)$ [KBr]	Other [KBr]	Chemical shift δ [$CDCl_3$]
$[(Ph_3P)_2(I)Pt(\mu\text{-}CS_2)Pt(I)PPh_3]$ **(3b)**	922m-s, 870m		7.4(Ph)
$[Pd(\eta^2\text{-}CS_2Et)(PPh_3)_2][BF_4]\cdot 0.5\ Et_2O$ **(4a)**	1165m	1055vs [$\nu(BF_4)$]	1.24(t,Me),3.33(q,SCH_2) (J 7.5 Hz) 7.2(Ph) [a]
$[Pd(\eta^2\text{-}CS_2Me)(PPh_3)_2]CF_3SO_3\cdot 0.5\ Et_2O$ **(4b)**	[b]	1270vs,1225m,1150s,1030s, 633s [$\nu(CF_3)$, $\nu(SO_3)$]	2.91(SMe),7.3(Ph) [a]
$[Pt(\eta^2\text{-}CS_2Et)(PPh_3)_2][BF_4]\cdot Et_2O$ **(5a)**	1130m	1055vs [$\nu(BF_4)$]	1.38(t,Me),3.37(q,SCH_2) (J 7.8 Hz) 7.25(Ph) [a]
$[Pt(\eta^2\text{-}CS_2Me)(PPh_3)_2]CF_3SO_3\cdot 0.5\ Et_2O$ **(5b)**	[c]	1270vs,1225m,1150s,1030s, 633s [$\nu(CF_3)$, $\nu(SO_3)$]	2.95(SMe),7.25(Ph) [a]
$[(Me_2PhP)_2(CO)_2Fe(SCS)Pt(Cl)(PPh_3)_2][BF_4]$ **(11a)**	1158m	2010vs,1956vs [$\nu(CO)$] [d] 1055vs [$\nu(BF_4)$]	1.55,1.62(2vt,Me) (J 9 Hz) 7.4(Ph)
$[(Ph_3P)_2(OC)_2Fe(SCS)Pt(Cl)(PPh_3)_2][BF_4]$ **(11b)**	1165m	2005vs,1953vs [$\nu(CO)$] [d] 1055vs [$\nu(BF_4)$]	7.4(Ph)

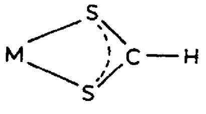
[a] Additional Et_2O-resonances (1.17, 3.44 ($J = 6.6$ Hz), rel. intensities corresp. to 5 and 10 H, resp.). [b] Assignment unclear due to bands of counteranion. [c] Located at 1133 cm^{-1} after exchange of anions with $NH_4[PF_6]$. [d] CH_2Cl_2 solvent.



(4a : M = Pd , R = Et , X = BF_4)
(4b : M = Pd , R = Me , X = CF_3SO_3)
(5a : M = Pt , R = Et , X = BF_4)
(5b : M = Pt , R = Me , X = CF_3SO_3)

2. *Protonation studies*

Dithioformiato (HCS_2) complexes (**6**) are best prepared by insertion of CS_2 into a metal hydride bond [20,21]. Such a synthesis of the isomeric (yet unreported) CS_2H complexes requires reverse metal and hydrogen polarities, as e.g. in the successive additions of CS_2 and H^+ to an electron-rich metal component. Our recent synthesis of $FpCS_2H$ (type **7a**) from {$Fp^-/CS_2/H^+$} demonstrates the validity of this synthetic concept [22]. Similarly, protonation by strong acids of the weakly basic *exo*-sulfur atom of η^2-CS_2 complexes should directly lead to the novel type **7b**-CS_2H compounds, though one might expect some instability due to their cationic nature.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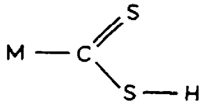
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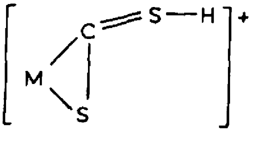

(7b)

This is definitely true in the case of [Pt(η^2-CS_2)(PPh_3)$_2$], for which no evidence could be obtained for an η^2-CS_2H intermediate. Instead, protonation with HCl in tetrahydrofuran at 25°C proceeds with total loss of CS_2 and formation of *trans*-[Pt(Cl)(H)(PPh_3)$_2$]. At 0°C in CH_2Cl_2, on the other hand, 50% of the CS_2 remain incorporated in the reaction product, which again turns out to be of the type [(Ph_3P)$_2$(Cl)Pt(μ-CS_2)Pt(PPh_3)$_2$]Cl. This result is strongly reminiscent of the first preparation of a platiniodithiocarboxylato(*S*,*S*′)-platinum complex attempting the synthesis of [Pt(Cl)(CS)(PPh_3)$_2$][BF_4] from [Pt(Cl)(C(S)OMe)(PPh_3)$_2$] and BF_3 [23].

Protonation studies of [Fe(η^2-CS_2)(CO)$_2$$L_2$] (L = PMe_2Ph, PPh_3) with trifluoroacetic acid have already been carried out, and shown to produce only CS_2-free [Fe($OOCCF_3$)$_2$(CO)$_2$$L_2$] (L = PMe_2Ph, PPh_3) with η^1-bound acetato ligands [24]. Careful examination of the stoichiometric reaction with "non-coordinating" etheral HBF_4 in benzene has now furnished evidence for the presence of a η^2-CS_2H group in

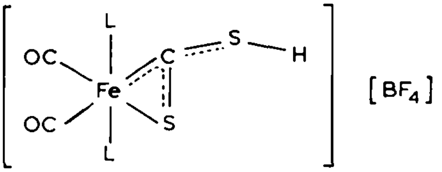
TABLE 2

CHARACTERISTIC IR ABSORPTIONS (CH_2Cl_2, cm^{-1}) OF **8a,b** [a]

8a		**8b**		Assignment
2490w-m		2460w, b [b]		ν(SH)
2027vs	(1990vs)	2025vs	(1993vs)	$\nu(CO)[A_1]$
1974vs	(1928vs)	1972vs	(1932vs)	$\nu(CO)[B_2]$
1130m	(1134s [b])	1140m [b]	(1147s [b])	ν(C=S)
1060vs		1060vs		$\nu(BF_4)$

[a] Corresponding absorptions of unprotonated form in parentheses. [b] In KBr.

the iron complexes. Shortly after addition of the acid to the red solution of $[Fe(\eta^2\text{-}CS_2)(CO)_2L_2]$, a slight lightening in colour is noticed; the orange solid which then separates out within a few minutes is extremely hygroscopic, and decomposes rapidly with evolution of CS_2 and H_2S. For L = PPh_3, the residue is mainly $[Fe(CO)_3(PPh_3)_2]$. Recrystallization or even extensive washing with ether, on the other hand, brings about deprotonation, regenerating $[Fe(\eta^2\text{-}CS_2)(CO)_2L_2]$, and so we were unable to obtain satisfactory analyses. The immediately recorded IR spectra, however, are in full accord with a formulation of the products as **8**. New weak to medium intensity bands appear between 2450 and 2500 cm^{-1}, i.e. in a region which is highly characteristic of SH stretching vibrations; the expected shift to higher wavenumbers of the ν(CO)-bands ($\overline{\Delta\nu(CO)} > 35$ cm^{-1}) also occurs (Table 2).



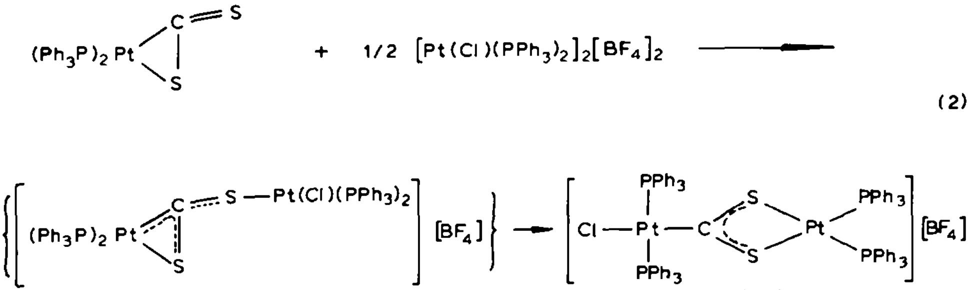
(8a : L = PMe_2Ph)
(8b : L = PPh_3)

The quality of the proton NMR spectra is limited by the lability of these compounds and only phenyl and methyl proton signals are observed; hydrido iron species, however, can be excluded with certainty.

3. Reactions with cationic metal complexes

We have shown previously that the 1/1 reaction of $[Pt(\eta^2\text{-}CS_2)(PPh_3)_2]$ with the cationic fragment $[Pt(Cl)(PPh_3)_2]^+$ provides the most obvious route to the platiniodithiocarboxylato(*S*,*S'*)platinum species **10** (eq. 2) [14,15].

A plausible step in its formation (as well as in the formation of other platiniodithiocarboxylatometal complexes) is electrophilic attack at the uncoordinated sulfur atom by the chloroplatinum species. This is substantiated by the addition of pentacarbonyl-chromium and -tungsten to $[Pt(\eta^2\text{-}CS_2)(PPh_3)_2]$ which, due to a particularly stable metal(**6a**) coordination sphere and the absence of

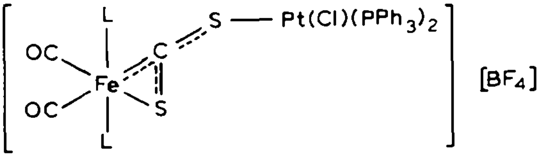

(9) (10)

(2)

halogen, stops at the η^2(C,S):η^1(S) bridging stage [14]. A related dinuclear metal complex has been synthesized from [Fe(η^2-CS_2)$(CO)_2(PMe_2Ph)_2$] and [Mn(η-C_5H_5)$(CO)_2$THF] and analyzed by X-ray diffraction [13]. Together with the homo- and hetero-dinuclear combinations Mn(SCS)Mn [25], Cr(SCS)Cr [26], W(SCS)W [19], Co(SCS)Cr [27,28], Co(SCS)Mn [27,28], Nb(SCS)W [29], Rh(SCS)Cr [27], Rh(SCS)Mn [27] and Fe(SCS)Mo [30], this constitutes a complete class of η^2(C,S): η^1(S)-CS_2-bridged complexes.

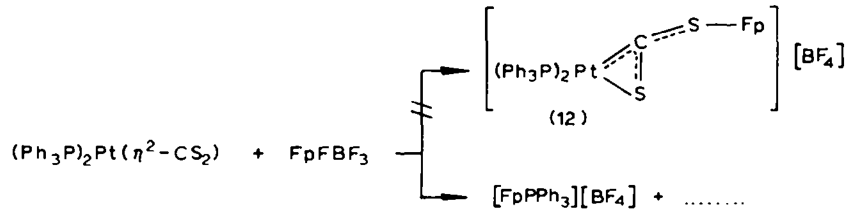
In a search for a more appropriate model for the assumed intermediate **9** we treated [Fe(η^2-CS_2)$(CO)_2L_2$] (L = PMe_2Ph, PPh_3) with 1/2[Pt(Cl)$(PPh_3)_2]_2[BF_4]_2$ at room temperature and immediately obtained yellow to orange solids with elementary analyses corresponding to the sum of the reactants. Significantly increased ν(CO)-frequencies along with comparatively little altered ν(C=S)-positions (Table 1) strongly favour an η^2(C,S): η^1(S)-type bridge.

The relative stability under mild conditions of the dinuclear complexes **11** certainly reflects the relative stability of the coordination sphere about iron even towards intrusion of the platinum bonded chloride. This higher stability of the ligand sphere of [Fe(η^2-CS_2)$(CO)_2(PR_3)_2$] compared with that of [Pt(η^2-


(11a : L = PMe_2Ph)
(11b : L = PPh_3)

CS_2)$(PPh_3)_2$] (cf. eq. 2) is also apparent in other electrophilic reactions (see above).

In this context, mention should be made of the reaction of [Pt(η^2-CS_2)$(PPh_3)_2$] with the halogen-free cation Fp^+. Here, instead of affording **12**, the expected isomer of [Fp(μ-CS_2)Pt$(PPh_3)_2$][BF_4] [14] (eq. 3a), break up of the platinum coordination sphere again occurs, with quantitative formation of $[FpPPh_3]^+$ together with some unidentified platinum species (eq. 3b).



(3a)

(3b)

Experimental

The ^{1}H NMR spectra were recorded on a JEOL JNM-PMX 60-spectrometer, the IR data were obtained with a Zeiss IMR 25-spectrophotometer, and the conductivities were determined using a WTW Model R 11-conductivity bridge. All experiments were performed under dry nitrogen by standard Schlenk-techniques. $[Pt(\eta^2\text{-}CS_2)(PPh_3)_2]$, $[Pd(\eta^2\text{-}CS_2)(PPh_3)_2]$, $[Fe(\eta^2\text{-}CS_2)(CO)_2L_2]$ and $[Pt(\mu\text{-}Cl)(PPh_3)_2]_2[BF_4]_2$ ($L = PMe_2Ph$, PPh_3) were prepared as described in the literature [1,5,31].

$[(Ph_3P)_2(I)Pt(\mu\text{-}CS_2)Pt(PPh_3)_2]I \cdot$ acetone (**3a**)

A stoichiometric amount of MeI was added to a benzene solution of $[Pt(\eta^2\text{-}CS_2)(PPh_3)_2]$. Within 10 min a deep-red colour had developed in the mixture, and this began to lighten after 1 h. Benzene was then removed in vacuo leaving a dark-yellow solid. The crude product was recrystallized from acetone/petroleum ether to give yellow crystals. Assignment of the above formula is based on IR (1720 [ν(CO-acetone)], 938 m, 874 m-s cm^{-1} [$\nu(CS_2)$]) and ^{1}H NMR (δ 7.35 [$P(C_6H_5)_3$], 2.10 ppm [$(CH_3)_2CO$]) as well as by comparison with analogous complexes prepared from $[Pt(\eta^2\text{-}CS_2)(PPh_3)_2]$ and $[PtX_2(PPh_3)_2]$ (X = Cl, Br) [16].

$[(Ph_3P)_2(I)Pt(\mu\text{-}CS_2)Pt(I)PPh_3]$ (**3b**)

Reaction of $[Pt(\eta^2\text{-}CS_2)(PPh_3)_2]$ with 1,2-diiodoethane and work-up as described for **3a** gave yellow crystals. Yield ~ 50%.

η^2-Dithioethoxycarbonylbis(triphenylphosphine)palladium tetrafluoroborate, $[Pd(\eta^2\text{-}CS_2Et)(PPh_3)_2][BF_4] \cdot 0.5\ Et_2O$ (**4a**)

0.58 g $[Pd(\eta^2\text{-}CS_2)(PPh_3)_2]$ (0.82 mmol) were dissolved in a mixture of 20 ml of CH_2Cl_2 and a few drops of CS_2, and a solution of a stoichiometric amount of $[Et_3O][BF_4]$ (0.16 g, 0.84 mmol) in CH_2Cl_2 was added dropwise by syringe. A gradual lightening of the dark-orange solution was noticed. After 30 min the solvent was removed, leaving a gummy mass which was stirred with diethyl ether. The ether was then decanted, and the resulting orange powder was dried in a high vacuum for 1 day at 50°C. The product was effectively pure, and the yield almost quantitative. Recrystallization at −30°C from CH_2Cl_2/Et_2O is possible, but this reduces the yield considerably due to extensive decomposition in solution.

η^2-Dithiomethoxycarbonylbis(triphenylphosphine)palladium trifluoromethylsulfonate, $[Pd(\eta^2\text{-}CS_2Me)(PPh_3)_2]CF_3SO_3 \cdot 0.5\ Et_2O$ (**4b**)

This was prepared from $[Pd(\eta^2\text{-}CS_2)(PPh_3)_2]$ (0.34 g, 0.48 mmol) and CF_3SO_2OMe (0.55 ml, 0.50 mmol) in a manner analogous to that used for **4a**.

TABLE 3

ANALYTICAL DATA AND PHYSICAL PROPERTIES

Compound	Colour	M.p. (°C) (dec.) uncorrected	Conductivity (acetone) [a]	mol. weight	Analysis (found (calc.) (%))	
					C	H
$[(Ph_3P)_2(I)Pt(\mu\text{-}CS_2)Pt(I)PPh_3]$ **(3b)**	yellow	> 280		1507.0	43.95 (43.84)	3.23 (3.01)
$[Pd(\eta^2\text{-}CS_2Et)(PPh_3)_2][BF_4]\cdot 0.5\ Et_2O$ **(4a)**	orange	> 120	125	860.1	57.29 (57.26)	4.70 (4.69)
$[Pd(\eta^2\text{-}CS_2Me)(PPh_3)_2]CF_3SO_3\cdot 0.5\ Et_2O$ **(4b)**	orange	> 110		908.3	52.80 (54.22)	4.20 (4.22)
$[Pt(\eta^2\text{-}CS_2Et)(PPh_3)_2][BF_4]\cdot Et_2O$ **(5a)** [b]	yellow	> 140	135	985.8	52.37 (52.39)	4.15 (4.60)
$[Pt(\eta^2\text{-}CS_2Me)(PPh_3)_2]CF_3SO_3\cdot 0.5\ Et_2O$ **(5b)**	yellow	> 130		997.0	49.43 (49.39)	3.79 (3.84)
$[(Me_2PhP)_2(OC)_2Fe(SCS)Pt(Cl)(PPh_3)_2][BF_4]$ **(11a)** [c]	yellow	116–120	134	1306.3	50.58 (50.57)	4.30 (4.01)
$[(Ph_3P)_2(OC)_2Fe(SCS)Pt(Cl)(PPh_3)_2][BF_4]$ **(11b)**	light-orange	139–142	137	1554.5	57.82 (57.95)	4.11 (3.89)

[a] $\Omega^{-1}\ mol^{-1}\ cm^2$. [b] S: Found 5.84, calcd. 6.50%. [c] P: Found 9.68, calcd. 9.48%.

η^2-Dithioethoxycarbonylbis(triphenylphosphine)platinum tetrafluoroborate, [Pt(η^2-CS_2Et)(PPh_3)$_2$][BF_4] · Et_2O (5a)

[Pt(η^2-CS_2)(PPh_3)$_2$] (0.50 g, 0.63 mmol) was dissolved in 20 ml CH_2Cl_2, and [Et_3O][BF_4] (0.13 g, 0.68 mmol) was added slowly with stirring. The reaction mixture soon turned orange and finally yellow. After 30 min **5a** was isolated by the procedure described for **4a**.

*η^2-Dithiomethoxycarbonylbis(triphenylphosphine)platinum trifluoromethylsulfonate, [Pt(η^2-CS_2Me)(PPh_3)$_2$]CF_3SO_3 · 0.5 Et_2O (**5b**)*

This was prepared from [Pt(η^2-CS_2)(PPh_3)$_2$] (0.62 g, 0.78 mmol) and CF_3SO_2OMe (0.90 ml, 0.82 mmol) in a manner analogous to that for **5a** and **4a**.

*η^2-Dithiohydroxycarbonyl(dicarbonyl)bis(triphenylphosphine)iron tetrafluoroborate, [Fe(η^2-CS_2H)(CO)$_2$(PPh_3)$_2$][BF_4] (**8b**)*

[Fe(η^2-CS_2)(CO)$_2$(PPh_3)$_2$] (0.52 g, 0.73 mmol) was suspended in benzene (40 ml), and 0.1 ml of a 54% solution of HBF_4 in ether was added dropwise with vigorous stirring. A slight lightening in color occurred. After 10 min the precipitate was filtered off and washed with a small amount of diethyl ether. More extensive washing causes deprotonation, regenerating the original complex. The residual ether was removed in vacuo leaving an orange solid in approximately 80% yield.

*η^2-Dithiohydroxycarbonyl(dicarbonyl)bis(dimethylphenylphosphine)iron tetrafluoroborate, [Fe(η^2-CS_2H)(CO)$_2$(PMe_2Ph)$_2$][BF_4] (**8a**)*

This was prepared in a manner analogous to that used for the preparation of **8b**. Intact **8a**, however, could only be identified in solution. Removal of the solvent and washing with ether left a reddish solid which, according to its IR spectrum (CH_2Cl_2: 2015, 1960 cm^{-1}) did not contain an SH group.

*[(Me_2PhP)$_2$(OC)$_2$Fe(SCS)Pt(Cl)(PPh_3)$_2$][BF_4](**11a**)*

This yellow complex was prepared from 325 mg [Fe(η^2-CS_2)(CO)$_2$(PMe_2Ph)$_2$] (0.70 mmol) and 590 mg [Pt(Cl)(PPh_3)$_2$]$_2$[BF_4]$_2$ (0.35 mmol) by a procedure analogous to that used for the preparation of **11b**. Yield: 0.75 g, 82% (crude product).

*[(Ph_3P)$_2$(OC)$_2$Fe(SCS)Pt(Cl)(PPh_3)$_2$][BF_4] (**11b**)*

A mixture of 0.40 g [Fe(η^2-CS_2)(CO)$_2$(PPh_3)$_2$] (0.56 mmol) and 0.47 g [Pt(Cl)(PPh_3)$_2$]$_2$[BF_4]$_2$ (0.28 mmol) was placed in a Schlenk tube and dissolved in 25 ml of dichloromethane. After 30 min the solution was poured into 150 ml of ether with stirring. A yellow to orange solid began to separate from the solution, and this was filtered off and washed with ether. Recrystallization of the crude product (0.80 g, 97%) from acetone/petroleum ether or from CH_2Cl_2/petroleum ether to give orange needles is possible, but at the cost of a substantial reduction in yield (30%).

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