Co-ordination Chemistry of Sulphines. Part 4.[1] Influence of the Phosphine Cone Angle on both the Oxidative Addition of Carbon–Sulphur and Carbon–Chlorine Side Bonds in [$Pt^0(PR_3)_2(XYC{=}S{=}O)$] Complexes and the (*E*)–(*Z*) Isomerization

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The co-ordination compounds [$Pt^0\{P(C_6H_{11})_3\}_2(C_{12}H_8CSO)$] (5a) ($C_{12}H_8CSO$ = fluorene-9-ylidenesulphine), [$Pt^0\{P(C_6H_{11})_3\}_2\{(E)$-(MeS)R'CSO\}] (*E*)-(5b), [$Pt^0\{P(C_6H_{11})_3\}_2\{(Z)$-(MeS)R'CSO\}] (*Z*)-(5b), [$Pt^0\{P(C_6H_{11})_3\}_2$-$\{(R'S)_2CSO\}$] (5c) (R' = *p*-MeC_6H_4), and [$Pt^0\{P(C_6H_{11})_3\}_2\{(E)$-(PhS)ClCSO\}] (*E*)-(5d') may be synthesized with retention of configuration from [$Pt^0(cod)_2$], $P(C_6H_{11})_3$, and the corresponding sulphines (cod = cyclo-octa-1,5-diene). The complexes (5a) and (5c) remain unchanged in $CDCl_3$ solution, while (*Z*)-(5b) isomerizes to (*E*)-(5b) and *vice versa*, until a 4 : 1 (*E*) : (*Z*) equilibrium is reached. The complex (*E*)-(5d') undergoes in $CDCl_3$ a fast oxidative addition of the C–Cl side bond, yielding the kinetically preferred *cis*-(*E*)-[$Pt^{II}Cl(PhSCSO)\{P(C_6H_{11})_3\}_2$] (*E*)-(6d'), which then isomerizes to the thermodynamically more stable *trans*-(*E*)- and -(*Z*)-[$Pt^{II}Cl(PhSCSO)\{P(C_6H_{11})_3\}_2$] (*E*)- and (*Z*)-(7d'). This shows that replacement of the PPh_3 ligands by the bulkier $P(C_6H_{11})_3$ ligands increases the barrier to intramolecular C–S oxidative addition. An overall mechanism for the intramolecular C–S oxidative-addition and reductive-coupling reactions on $Pt(PR_3)_2$ centres (R = C_6H_{11} or Ph) and the (*E*)–(*Z*) isomerization of co-ordinated sulphines and metal-substituted sulphines (oxidative-addition products) is put forward.

SULPHINES, XYC=S=O, have a bent planar structure[2-7] and are heterocumulenes;[2-7] they are related to sulphinylanilines (aryl–N=S=O) and diarylsulphurdi-imines (aryl–N=S=N–aryl), the chemistry of which is being studied in our laboratory.[8,9]

Recently, we studied the oxidative-addition reaction of the C–Cl and C–S side bonds of sulphines which were η^2-CS co-ordinated to $Pt^0(PPh_3)_2$.[1,10-13] We found that the complexes [$Pt^0(PPh_3)_2\{(E)$-(MeS)R'CSO\}] † (*E*)-(2b), [$Pt^0(PPh_3)_2\{(Z)$-(MeS)R'CSO\}] (*Z*)-(2b), and [Pt^0-$(PPh_3)_2\{(R'S)_2CSO\}$] (2c) (R' = *p*-MeC_6H_4) were converted into their corresponding oxidative-addition products *cis*-(*E*)- and -(*Z*)-[$Pt^{II}(MeS)(R'CSO)(PPh_3)_2$] (*E*)- and (*Z*)-(3b), and *cis*-(*E*)- and -(*Z*)-[$Pt^{II}(R'S)(R'SCSO)$-$(PPh_3)_2$] (*E*)- and (*Z*)-(3c).[1,11-13] The structures of these complexes are shown in Figure 1. We have already deduced that the oxidative additions of these C–S side bonds proceed *via* an intramolecular process involving formation of η^3-SCS co-ordinated intermediates.[1,12] Furthermore, both the η^2-CS-co-ordination compounds and their oxidative-addition products undergo in solution (*E*)–(*Z*) sulphine isomerization.

In solution the η^2-CS co-ordination complex [Pt^0-$(PPh_3)_2\{(E)$-(R'S)ClCSO\}] (*E*)-(2d) undergoes a fast oxidative addition of the C–Cl side bond yielding *cis*-(*E*)-, -(*Z*)-, *trans*-(*E*)-, and -(*Z*)-[$Pt^{II}Cl(R'SCSO)(PPh_3)_2$] (*E*)-, (*Z*)-(3d), (*E*)- and (*Z*)-(4d) (R' = *p*-MeC_6H_4) (see Figure 1). No mechanism for this oxidative-addition process has been deduced.[1]

An important consequence of the oxidative-addition reaction is the increase of steric interaction between the *cis* PR_3 ligands in the platinum–sulphine complexes. The P–Pt–P angle decreases *ca.* 10°, as has been illustrated by *X*-ray crystal-structure analyses of [$Pt^0(PPh_3)_2(C_{12}H_8CSO)]\cdot0.5C_6H_6$[12] ($C_{12}H_8CSO$ = fluorene-

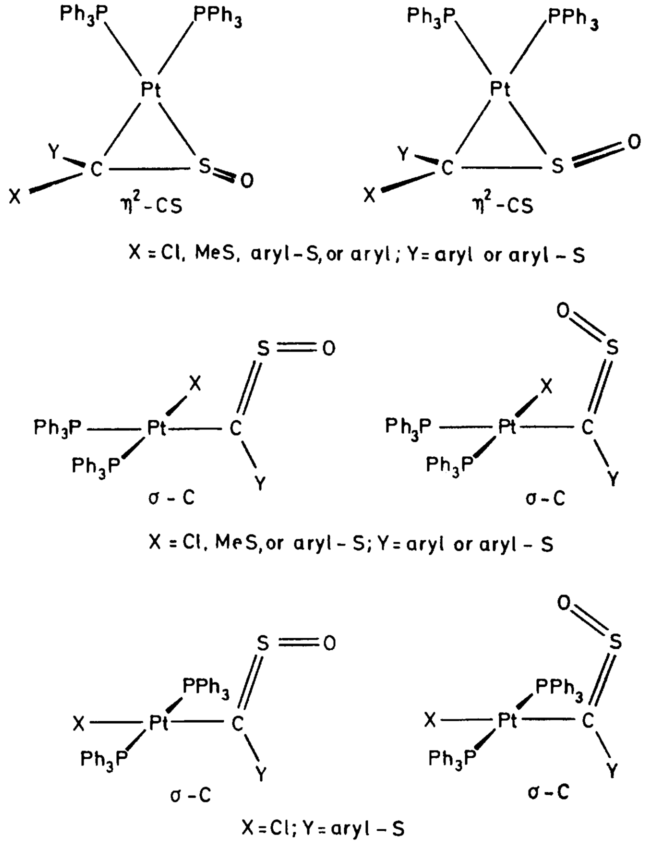

FIGURE 1 Structures of η^2-CS co-ordinated platinum-sulphine complexes and their σ-C co-ordinated oxidative-addition products

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† (*E*) and (*Z*) refer to the configuration of the sulphine C=S bond. If these are placed inside the molecular formula this indicates that the sulphine has the (*E*) or (*Z*) configuration and is co-ordinated as such (η^2-CS, σ-S, or η^3-SCS). If these are placed before the molecular formula, this indicates that the PtXC=S=O entity as a whole has the (*E*) or (*Z*) configuration, with σ-C co-ordination.

9-ylidenesulphine) (2a) [P–Pt–P = 106.45(5)°] and *cis*-(*E*)-[Pt^{II}(PhS)(PhSCSO)(PPh_3)$_2$]·C_6H_6 [1] (*E*)-(3c′) [P–Pt–P = 96.9(1)°], which are representatives of η^2-CS co-ordination compounds and oxidative-addition products (metal-substituted sulphines) respectively.

We have now introduced the bulky $P(C_6H_{11})_3$ phosphine [14] as co-ligand in platinum–sulphine complexes, in place of the smaller PPh_3. This should increase the barrier to oxidative addition and it is anticipated [1,12] that such reactions will be slowed down or even blocked. This should allow further study of the mechanism of the (*E*)–(*Z*) isomerization and its relation to the oxidative-addition reaction.

EXPERIMENTAL

The i.r. spectra were recorded on a Perkin-Elmer 283 spectrophotometer. The ^1H n.m.r. spectra were recorded on a Bruker WM250 and the ^{31}P-{^1H} n.m.r. spectra on a Varian XL100 spectrometer. Elemental analyses were carried out by the Analytical Section of the Institute for Organic Chemistry TNO, Utrecht, The Netherlands. Molecular weights were determined in $CHCl_3$ with a Hewlett–Packard (model 320B) vapour-pressure osmometer.

The sulphines $C_{12}H_8C{=}S{=}O$ (1a), (*E*)- and (*Z*)-(MeS)(*p*-MeC_6H_4)C=S=O, (*E*)- and (*Z*)-(1b), (*p*-MeC_6H_4S)$_2$C=S=O (1c), and (*E*)-(PhS)ClC=S=O (*E*)-(1d′) were prepared according to literature procedures.[15,16] The compound [Pt^0(cod)$_2$] (cod = cyclo-octa-1,5-diene) was obtained from Emser Werke A.G., Switzerland and was purified before use (see below). All the complexes [Pt^0{$P(C_6H_{11})_3$}$_2$(XYCSO)] were prepared under an N_2 atmosphere using Schlenk apparatus.

(*i*) [Pt^0{$P(C_6H_{11})_3$}$_2$($C_{12}H_8CSO$)] (5a).—The compound [Pt^0(cod)$_2$] (0.5 mmol) was stirred in toluene (10 cm^3). Ethylene was passed through the suspension until almost all the solid was dissolved by formation of [$Pt^0(C_2H_4)_3$].[17] The solution was filtered to remove impurities and $P(C_6H_{11})_3$ (1.0 mmol) was added, followed by slow addition of (1a) in toluene (3 cm^3) after almost all the $P(C_6H_{11})_3$ had dissolved. The reaction mixture was stirred for *ca.* 1.5 h. The white precipitate was filtered off, washed with n-pentane, and dried *in vacuo*. (If no precipitate was formed, the solvents were removed *in vacuo* and n-pentane was added to the residue. The precipitate was then filtered off and dried *in vacuo*.) Yield *ca.* 40% {calculated on crude [Pt^0(cod)$_2$]} (Found: C, 60.4; H, 7.8; P, 6.1; S, 3.2%; *M*, 912. Calc. for $C_{49}H_{74}OP_2PtS$: C, 60.8; H, 7.70; P, 6.40; S, 3.30%; *M*, 968).

(*ii*) [Pt^0{$P(C_6H_{11})_3$}$_2${(*E*)-(MeS)(*p*-MeC_6H_4)CSO}](*E*)-(5b).*—The procedure was similar to the above, using n-pentane (25 cm^3) as solvent for [Pt^0(cod)$_2$] and a mixture of n-pentane and toluene (3 cm^3) for (*E*)-(1b). The reaction mixture was cooled to 0 °C before addition of (*E*)-(1b) and stirred for 1.5 h at 0 °C. Yield *ca.* 30% (Found: C, 55.9; H, 8.2; P, 6.3; S, 5.9%. Calc. for $C_{45}H_{76}OP_2PtS_2$: C, 56.65; H, 8.05; P, 6.50; S, 6.70%).

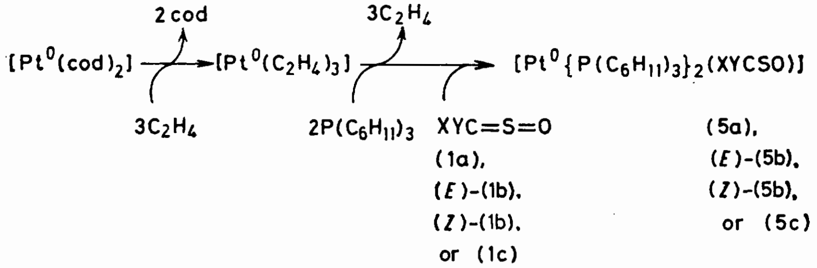
(*iii*) [Pt^0{$P(C_6H_{11})$}$_2${(*Z*)-MeS)(*p*-MeC_6H_4)CSO}](*Z*)-(5b).*—The procedure was similar to (*ii*), with cooling to −10 °C. Yield *ca.* 40% (Found: C, 56.8; H, 8.3; P, 5.9; S, 5.6. Calc. for $C_{45}H_{76}OP_2PtS_2$: C, 56.65; H, 8.05; P, 6.50; S, 6.70%).

(*iv*) [Pt^0{$P(C_6H_{11})_3$}$_2${(*p*-MeC_6H_4S)$_2$CSO}] (5c).*—The procedure was similar to (*i*), using n-pentane (25 cm^3) as solvent for [Pt^0(cod)$_2$]. The reaction mixture was cooled to −20 °C before addition of (1c) and stirred for 1.5 h at −20 °C. Yield *ca.* 40% (Found: C, 58.0; H, 7.8; S, 8.3%; *M*, 990. Calc. for $C_{51}H_{80}OP_2PtS_3$: C, 57.65; H, 7.60; S, 9.05%; *M*, 1 062).

(*v*) [Pt^0{$P(C_6H_{11})_3$}$_2${(*E*)-(PhS)ClCSO}](*E*)-(5d′).—The procedure was similar to (*i*), using toluene (20 cm^3) or n-pentane (25 cm^3) as solvent for [Pt^0(cod)$_2$]. The reaction mixture was cooled to 0 °C before addition of (*E*)-(1d′) and stirred for 1.5 h at 0 °C. A mixture of (*E*)-(5d′) and -(6d′) was obtained. Yield *ca.* 25% (Found: C, 53.3; H, 7.5; Cl, 3.6; P, 6.2; S, 6.2. Calc. for $C_{42}H_{71}ClOP_2PtS_2$: C, 53.75; H, 7.45; Cl, 3.70; P, 6.45; S, 6.70%).

RESULTS

(*i*) *Synthesis and Characterization of the* η^2-CS *Co-ordination Complexes* [Pt^0{$P(C_6H_{11})_3$}$_2$(XYCSO)] [XY = $C_{12}H_8$ (5a); X = MeS, Y = *p*-MeC_6H_4 (*E*)- *and* (*Z*)-(5b); X = Y = *p*-MeC_6H_4S (5c)].—The complexes [Pt^0{$P(C_6H_{11})_3$}$_2$($C_{12}H_8CSO$)] (5a), [Pt^0{$P(C_6H_{11})_3$}$_2${(*E*)-(MeS)R′CSO}] (*E*)-(5b), [Pt^0{P-(C_6H_{11})$_3$}$_2${(*Z*)-(MeS)R′CSO}] (*Z*)-(5b), and [Pt^0{P-(C_6H_{11})$_3$}$_2${(*p*-MeC_6H_4S)$_2$CSO}] (5c) (R′ = *p*-MeC_6H_4) were obtained from the reaction of [Pt(cod)$_2$] with $P(C_6H_{11})_3$ (2 mol) and the corresponding sulphine (1 mol) $C_{12}H_8C{=}S{=}O$ (1a), (*E*)- and (*Z*)-(MeS)R′C=S=O (*E*)- and (*Z*)-(1b), and (R′S)$_2$C=S=O (1c) according to equation (1).



(1)

In these $P(C_6H_{11})_3$ complexes the sulphines are η^2-CS co-ordinated, as concluded from a comparison of their i.r. and ^{31}P n.m.r. data with those of the corresponding PPh_3 complexes (2a), (*E*)-, (*Z*)-(2b), and (2c) for which η^2-CS co-ordination has already been established [10,12] (see Table). The present complexes each show one ν(CSO) absorption

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* The analytical data for S and P are not satisfactory because of the presence of impurities [*e.g.* originating from the Pt(cod)$_2$ used]. Recrystallization was not successful because of high solubility of the compound in organic solvents as well as of the limited stability in solution. However, its formulation is undoubtedly proven by comparison of its spectroscopic data with those of the corresponding PPh_3 compounds.

Spectroscopic data

	Compound	R	I.r.[a] ν(CSO)/ cm^{-1}	^{31}P n.m.r.[b] ^1J(Pt–P$_a$)/ Hz	^1J(Pt–P$_b$)/ Hz	^2J(P$_a$–P$_b$)/ Hz	δ(P$_a$)[c]/ p.p.m.	δ(P$_b$)[c]/ p.p.m.	^{1}H n.m.r.[b] δ(H$_o$)[d,e]/ p.p.m.	δ(H$_m$)[d,f]/ p.p.m.	^3J(H$_o$–H$_m$)/ Hz	δ(H$_s$)[d,g]/ p.p.m.	δ(H$_t$)[d,h]/ p.p.m.	Ref.
(5a)	[Pt^0(PR$_3$)$_2$(C$_{12}$H$_8$CSO)]	C$_6$H$_{11}$	1 004	3 425	3 325	15	28.8	28.8	*i*	*i*	*i*			*j*
(2a)		Ph	1 006	3 561	3 491	11	23.4	20.6	7.85	*i*	*i*			10
(*E*)-(5b)	[Pt^0(PR$_3$)$_2${(*E*)-(MeS)R′CSO}] [k]	C$_6$H$_{11}$	1 005	3 449	3 317	15	27.2	25.8	7.81	7.10	6.8	2.32	2.27	*j*
(*E*)-(2b)		Ph	1 006	3.675	3 419	13	21.6	19.9	*i*	*i*	*i*	2.25	2.25	10
(*Z*)-(5b)	[Pt^0(PR$_3$)$_2${(*Z*)-(MeS)R′CSO}] [k]	C$_6$H$_{11}$	1 000	3 380	3 264	13	27.5	26.0	7.26	6.96	8.1	2.24	2.24	*j*
(*Z*)-(2b)		Ph	1 010	3 603	3 345	11	20.5	19.6	*i*	*i*	*i*	2.20	2.25	10
(5c)	[Pt^0(PR$_3$)$_2${(R′S)$_2$CSO}] [k]	C$_6$H$_{11}$	1 016	3 475	3 470	12	26.9	27.7	7.34, 7.10	6.58, 6.57	8.4, 8.4		2.15, 2.13	*j*
(2c)		Ph	1 012	3 602	3 523	8	20.5	19.5	*i*	*i*	*i*		2.35, 2.30	10
(*E*)-(5d′)	[Pt^0(PR$_3$)$_2${(*E*)-(PhS)ClCSO}]	C$_6$H$_{11}$	1 003	*l*	*l*	*l*		*l*	*l*	*l*	*l*			*j*
(*E*)-(2d′)		Ph	1 017	3 539	3 343	7	20.6	18.1	*i*	*i*	*i*			10
(*E*)-(6d′)	*cis*-(*E*)-[Pt^{II}Cl(PhSCSO)(PR$_3$)$_2$]	C$_6$H$_{11}$	1 079, 945	3 718	2 268	15	16.4	12.4	*l*	*l*	*l*			*j*
(*E*)-(3d)	*cis*-(*E*)-[Pt^{II}Cl(R′SCSO)(PR$_3$)$_2$] [k]	Ph	1 080, 949	3 892	2 285	18	12.4	17.4	*i*	*i*	*i*		2.63	
(*E*)-(7d′)	*trans*-(*E*)-[Pt^{II}Cl(PhSCSO)(PR$_3$)$_2$]	C$_6$H$_{11}$	*l*	2 396			14.6		*l*	*l*	*l*			*j*
(*E*)-(4d)	*trans*-(*E*)-[Pt^{II}Cl(R′SCSO)(PR$_3$)$_2$] [k]	Ph	*l*	2 738			19.9		*i*	*i*	*i*		2.50	*l*
(*Z*)-(7d′)	*trans*-(*Z*)-[Pt^{II}Cl(PhSCSO)(PR$_3$)$_2$]	C$_6$H$_{11}$	*l*	2 485			17.5		*l*		*l*			*j*
(*Z*)-(4d)	*trans*-(*Z*)-[Pt^{II}Cl(R′SCSO)(PR$_3$)$_2$] [k]	Ph	*l*	2 805			22.8		*i*	*i*	*i*		2.22	*l*

[a] KBr mull. [b] In CDCl$_3$. [c] Relative to H$_3$PO$_4$ (85%), positive is downfield. [d] Relative to SiMe$_4$, internal reference. [e] *ortho* Protons. [f] *meta* Protons. [g] MeS Protons. [h] *p*-MeC$_6$H$_4$ alkyl protons. [i] Not assigned. [j] This work. [k] R′ = *p*-MeC$_6$H$_4$. [l] Not measured.

at *ca.* 1 005 cm^{-1} and two inequivalent ^1J(Pt–P) values between 3 475 and 3 264 Hz.

The ^{1}H n.m.r. spectra showed AB resonance patterns for the aryl protons of (*E*)-, (*Z*)-(5b), and (5c); for the latter complex two inequivalent Me signals were observed (see Table). The *ortho* protons in (5a) and (*Z*)-(5b) were not shifted downfield to 10—11 p.p.m. as was found for the *ortho* protons *syn* to Rh in the σ-S co-ordinated rhodium–sulphine complexes *trans*-[Rh^{I}Cl(PR$_3$)$_2$(C$_{12}$H$_8$CSO)] (R = C$_6$H$_{11}$ or Pr^i),[18] therefore excluding the presence of σ-S co-ordinated sulphine.

The ^{31}P n.m.r. spectra of the precipitated products from the reaction of [Pt^0(cod)$_2$] and P(C$_6$H$_{11}$)$_3$ with either pure (*E*)- or pure (*Z*)-(1b) showed in each case only one AB resonance pattern (complete with Pt satellites). However, the different chemical-shift positions indicate that the configuration of the sulphines is retained upon co-ordination to Pt^0{P(C$_6$H$_{11}$)$_3$}$_2$, *i.e.* (*E*)-(1b) yielded only (*E*)-(5b) and (*Z*)-(1b) only (*Z*)-(5b). The same retention of configuration was found in the synthesis of the corresponding PPh$_3$ complexes (*E*)- and (*Z*)-(2b).[10]

(*ii*) *Study of the Stability of* [Pt^0{P(C$_6$H$_{11}$)$_3$}$_2$(XYCSO)] {(5a), (*E*)-, (*Z*)-(5b) *and* (5c)} *towards Intramolecular* C–S *Oxidative Addition and* (*E*)–(*Z*) *Isomerization.*—The complexes (5a), (5c), (*E*)-, and (*Z*)-(5b) were dissolved in CDCl$_3$ at room temperature and ^{31}P n.m.r. spectra were recorded as a function of time.

Complex (5a) remained unchanged for at least 3 days. The same stability has been found for the corresponding PPh$_3$ complex (2a).[10-12] Similarly, no conversion of (5c) was observed after 48 h, although a few low-intensity unassignable resonances were observed. By contrast, the corresponding PPh$_3$ complex (2c) was completely converted, under the same conditions, into the oxidative-addition stereoisomers (*E*)- and (*Z*)-(3c).[1,11,13]

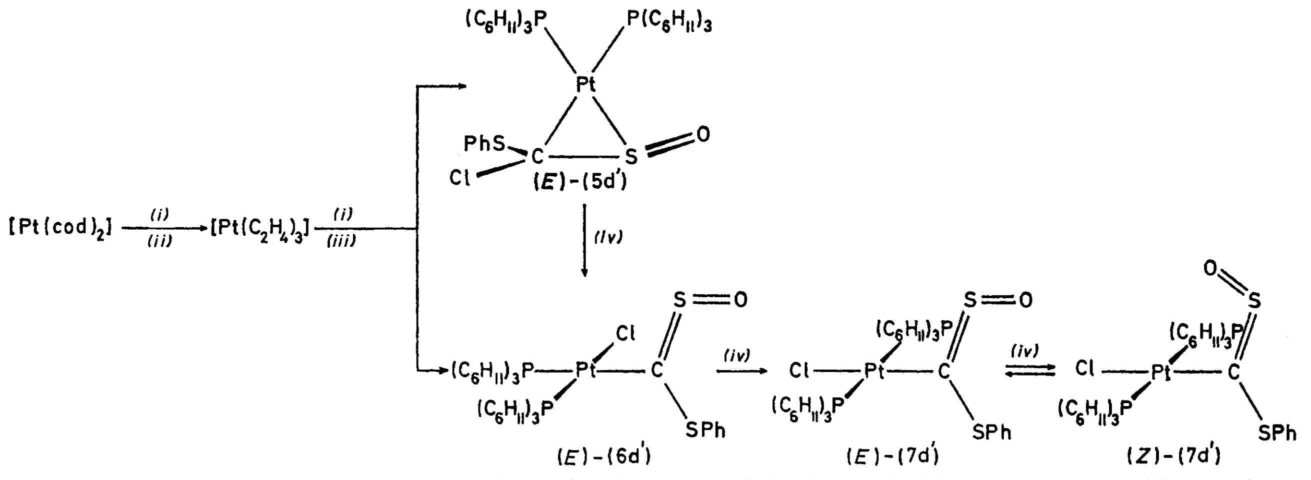

FIGURE 3 Synthesis and conversion of [Pt^0{P(C$_6$H$_{11}$)$_3$}$_2${(*E*)-(PhS)ClCSO}] (*E*)-(5d′). (*i*) Toluene or n-pentane; (*ii*) +3C$_2$H$_4$, −2 cod; (*iii*) (i) + 2P(C$_6$H$_{11}$)$_3$, (ii) +(*E*)-(1d′), −3C$_2$H$_4$; (*iv*) in CDCl$_3$

Dissolution of (*Z*)-(5b) resulted in a slow conversion of this complex into (*E*)-(5b) until an equilibrium mixture of *ca.* 4 : 1, (*E*) : (*Z*) molar ratio was reached. The same mixture, which reached equilibrium after *ca.* 36 h, could be obtained by starting from (*E*)-(5b). However, after 48 h significantly more impurities were present in both reaction mixtures compared to an aged solution of (5c), where the impurities were not oxidative-addition products. The corresponding PPh$_3$ complexes (*E*)- and (*Z*)-(2b) were converted within 36 h under the same conditions into an equilibrium mixture consisting of (*E*)-(2b) and the oxidative-addition stereoisomers (*E*)- and (*Z*)-(3b) in a *ca.* 1 : 1 : 1 molar ratio, while traces of (*Z*)-(2b) were present.[12,13]

No significant change in the rate of isomerization of (*Z*)- into (*E*)-(5b) was detected upon raising the concentration of the starting stereoisomer two-fold, indicating that the (*E*)-(*Z*) isomerization proceeds by an intramolecular mechanism. Similarly, the interconversion of (*E*)- and (*Z*)-(2b) showed no concentration dependency.[12,13]

Apparently, the intramolecular C–S oxidative-addition reaction observed for the PPh$_3$ complexes (2c), (*E*)- and (*Z*)-(2b) does not occur for the corresponding P(C$_6$H$_{11}$)$_3$ complexes (5c), (*E*)- and (*Z*)-(5b). The complex (5c) remains stable in CDCl$_3$ solution whilst (*Z*)-(5b) only isomerizes intramolecularly into (*E*)-(5b) and *vice versa* (see Figure 2).

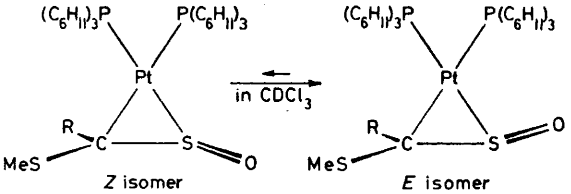

FIGURE 2 Isomerization of [Pt^0{P(C$_6$H$_{11}$)$_3$}$_2${(*E*)-(MeS)(*p*-MeC$_6$H$_4$)CSO]} (*E*)-(5b) and [Pt^0{P(C$_6$H$_{11}$)$_3$}$_2${(*Z*)-(MeS)-(*p*-MeC$_6$H$_4$)CSO}] (*Z*)-(5b)

(*iii*) [Pt^0{P(C$_6$H$_{11}$)$_3$}$_2${(*E*)-(PhS)ClCSO}] (*E*)-(5d′): *Synthesis, Characterization, and Reactivity towards Oxidative Addition.*—The reaction of [Pt^0(cod)$_2$] and P(C$_6$H$_{11}$)$_3$ with (*E*)-(PhS)ClC=S=O (*E*)-(1d′) (1 : 2 : 1 molar ratio) in n-pentane or toluene resulted in the precipitation of a white solid. Infrared spectra (KBr mull) of this product revealed three absorptions (1 070 m, 1 025m, and 945m cm^{-1}) assignable to ν(CSO). The absorption at 1 025 cm^{-1} points to the η^2-CS co-ordination complex [Pt^0{P(C$_6$H$_{11}$)$_3$}$_2${(*E*)-(PhS)Cl-CSO}] (*E*)-(5d′) [see section (*i*); the ν(SO) absorption of the corresponding PPh$_3$ complex (*E*)-(2d′) was found at 1 017 cm^{-1} (see Table) [10]]. The two further ν(CSO) absorptions (*i.e.* 1 070 and 945 cm^{-1}) indicated that *cis*- and/or *trans*-(*E*)-[Pt^{II}Cl(PhSCSO){P(C$_6$H$_{11}$)$_3$}$_2$] (*E*)-(6d′) and/or -(7d′)

were also present in the precipitate. These ν(CSO) absorptions are similar to those of the PPh_3 complex (*E*)-(3d′). The ^{31}P n.m.r. spectrum of the white precipitate was recorded directly after dissolution in $CDCl_3$. The $^1J(Pt-P)$ values of 2 268 and 3 718 Hz can be assigned to P atoms *trans* to C and Cl atoms respectively.[19–22] The absence of (*E*)-(5d′) in this spectrum is a result of the very fast oxidative addition of the C–Cl side bond to the $Pt^0\{P(C_6H_{11})_3\}_2$ unit resulting in formation of (*E*)-(6d′). Previously, a very fast oxidative addition in $CDCl_3$ of the C–Cl side bond of (*E*)-(2d′) to the Pt^0 unit resulting in formation of (*E*)-(3d′) was found.[1] Within 2 days the ^{31}P n.m.r. spectrum of (*E*)-(6d′) showed a resonance pattern at 14.6 p.p.m. and later on also one at 17.5 p.p.m., which are due to *trans*-(*E*)- and -(*Z*)-$[Pt^{II}Cl(PhSCSO)\{P(C_6H_{11})_3\}_2]$ (*E*)- and (*Z*)-(7d′), respectively, deduced by comparison of the ^{31}P n.m.r. data with those of *trans*-(*E*)- and -(*Z*)-$[Pt^{II}Cl(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]$ (*E*)- and -(*Z*)-(4d) (see Table). In particular the $^1J(Pt-P)$ values could be ascribed to P atoms *trans* to P atoms.[19, 20, 23–25] On going from (*E*)- to (*Z*)-(7d′) a downfield shift of 2.9 p.p.m. and an increase of $^1J(Pt-P)$ of 89 Hz was found. Similar changes are generally found for P atoms co-ordinated *cis* with respect to the C atom of the sulphine group on going from (*E*) to (*Z*) oxidative-addition products.[1]

Apparently, the reactions of $[Pt^0(cod)_2]$ and $P(C_6H_{11})_3$ with (*E*)-(1d′) in n-pentane or toluene yielded a mixture of (*E*)-(5d′) and -(6d′). Because of the lability of the C–Cl side bond towards oxidative addition to Pt^0, (*E*)-(5d′) is already partly converted into (*E*)-(6d′) during the synthesis and dissolution in $CDCl_3$ causes the immediate conversion of the remaining (*E*)-(5d′) into -(6d′). The same phenomenon is found for the corresponding PPh_3 system.[1] Because of the bulky $P(C_6H_{11})_3$ ligands the *cis* product (*E*)-(6d′) is less favoured then the *trans* product (*E*)-(7d′) into which it slowly isomerizes. The latter complex slowly undergoes (*E*)–(*Z*) isomerization, forming (*Z*)-(7d′); similar behaviour was found previously for the corresponding PPh_3 complexes (*E*)- and (*Z*)-(4d). These results are summarized in Figure 3.

DISCUSSION

(*i*) *The Influence of the Bulkiness of the Phosphines on the Oxidative Addition of* C–S *and* C–Cl *Side Bonds of Sulphines,* η^2-CS *Co-ordinated to* Pt^0.

—In order to study the influence of the bulkiness of the phosphines on the oxidative-addition reaction of C–S and C–Cl side bonds of sulphines, η^2-CS co-ordinated to Pt^0, the $P(C_6H_{11})_3$ complexes (5a), (*E*)-, (*Z*)-(5b), (5c), and (*E*)-(5d′) were synthesized and their reactivity compared with that of the corresponding PPh_3 complexes, (2a), (*E*)-, (*Z*)-(2b), (2c), and (*E*)-(2d′).

A good parameter for the bulkiness of phosphines is the cone angle θ. Using molecular models the cone angles of $P(C_6H_{11})_3$ and PPh_3 were found to be 179 and 145° respectively.[14] From crystallographic data it was found that the phosphines can be described as cog-like cones, which can give good intermeshing in the case of more than one phosphine co-ordinated to the metal.[26–29] Cone-angle and ligand-profile calculations revealed that in complexes where two or three $P(C_6H_{11})_3$ groups are attached to one metal atom the cyclohexyl orientations change to decrease the cone angle, *e.g.* $[Pt^0\{P(C_6H_{11})_3\}_3]$: $\theta = 164°$ [crowded $P(C_6H_{11})_3$] and $[\{Hg[P(C_6H_{11})_3](NO_3)_2\}_2]$: $\theta = 181°$ [uncrowded $P(C_6H_{11})_3$].

Both the PPh_3 and $P(C_6H_{11})_3$ complexes (2a) [10] and (5a) were found to be stable in $CDCl_3$, which is as expected, because reactive side bonds in the sulphines in these complexes are absent. The increase of the bulkiness on going from PPh_3 to $P(C_6H_{11})_3$ as co-ligands should, at least, be partly compensated by a reduction of the cone angle of the $P(C_6H_{11})_3$ (see above) and perhaps a small increase of the P–Pt–P angle.

A significant difference in reactivity, which obviously depends on the phosphine ligand present, is observed, when C–S side bonds are present in the sulphine, *cf.* the stable complex (5c) and unstable (2c). In our opinion this can shed light on the mechanism operative in these oxidative-addition reactions. The absence of the oxidative-addition reaction of (5c), (*E*)-, and (*Z*)-(5b) can be explained in terms of the intramolecular mechanism, already deduced for the PPh_3 complexes (2c),[1] (*E*)-, and (*Z*)-(2b).[12] The intramolecular C–S oxidative addition is thought to proceed *via* a gliding of the $Pt^0(PPh_3)_2$ unit along the S–C=S frame resulting in formation of an η^3-SCS co-ordinated intermediate or transition state. Extended gliding to the C–S side bond is then followed by oxidative addition of this bond. In the PPh_3 complexes the P–Pt–P angle has to diminish *ca.* 10° on going from Pt^0 to Pt^{II} (see Introduction). It is obvious that for a phosphine with a larger cone angle the energy for this process will increase. It appears that the introduction of the more bulky $P(C_6H_{11})_3$ co-ligands increases this barrier to such an extent that C–S oxidative addition does not occur at room temperature.*

It is not surprising that C–Cl oxidative addition occurs both for the $P(C_6H_{11})_3$ complex (*E*)-(5d′) and for the PPh_3 complex (*E*)-(2d′).[1] The greater reactivity of the C–Cl bonds compared to the C–S bonds with respect to oxidative addition to Pt^0 is well documented.[1, 30–32] No mechanism could be deduced for the C–Cl oxidative addition in the case of the PPh_3 complex (*E*)-(2d).[1] The conversion of (*E*)-(5d′) into the *cis* complex (*E*)-(6d′) must involve an increase in the oxidative-addition barrier owing to the larger $P(C_6H_{11})_3$ cone angle. However, this barrier which is comparatively much lower for the C–Cl than the C–S side bond, is not sufficiently increased by introducing the more bulky $P(C_6H_{11})_3$ groups to prevent the reaction. The formation of the *cis* complex (*E*)-(6d′) is kinetically controlled, because the thermodynamically more stable *trans* isomer (*E*)-(7d′) is the final reaction product [excepting (*E*)–(*Z*) isomerization]. In the latter *trans* product the steric interaction between the bulky $P(C_6H_{11})_3$ groups is minimal. How-

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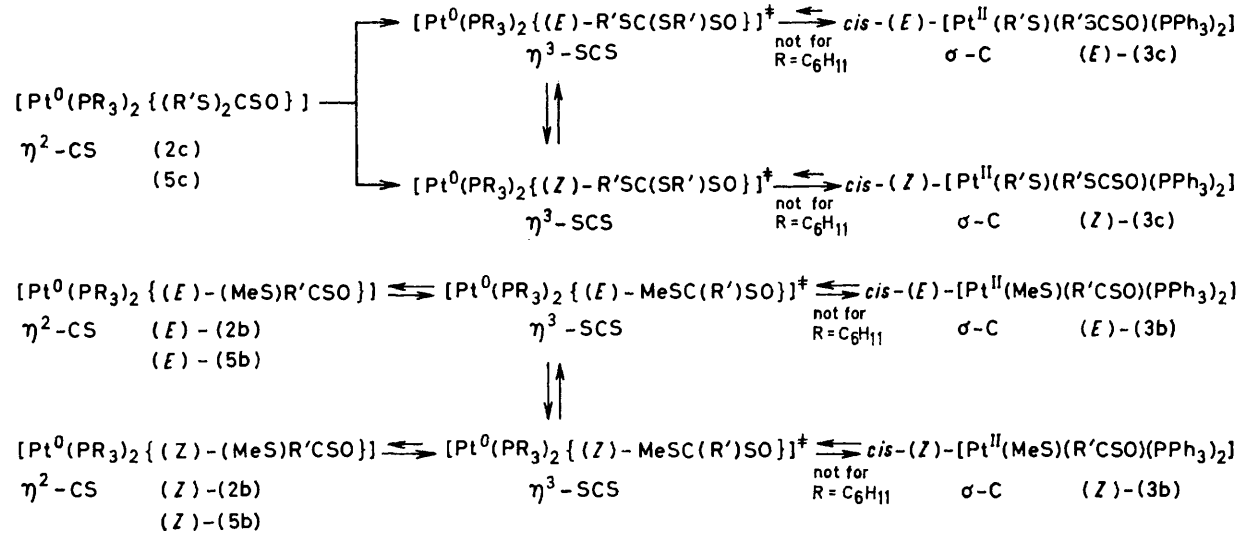
* Preliminary studies showed that the reaction of $K[SC_6H_4\text{-}OMe\text{-}p]$ with *cis*-(*E*)-$[Pt^{II}Cl(PhSCSO)\{P(C_6H_{11})_3\}_2]$ yielded a mixture of the two possible η^2-CS co-ordination complexes $[Pt^0\{P(C_6H_{11})_3\}_2\{(PhS)(p\text{-}MeOC_6H_4S)CSO\}]$, instead of the expected oxidative-addition stereoisomers *cis*-(*E*)- and -(*Z*)-$[Pt^{II}(p\text{-}MeOC_6H_4S)(PhSCSO)\{P(C_6H_{11})_3\}_2]$. This result indicates that the intramolecular C–S oxidative addition, in the case of $R = C_6H_{11}$, is not only kinetically blocked but also thermodynamically unfavourable.

ever, *cis* positioned $P(C_6H_{11})_3$ ligands have been observed in square-planar complexes, *e.g.* the platinum–hydrido-complex, $[Pt^{II}(H)\{P(C_6H_{11})_3\}_3]^+$.[27] In this complex the small hydrido-ligand allows bending of the P–Pt–P angle in the direction of the hydride. Likewise, the $(R'SCSO)^-$ ligand represents a ligand with minimal steric bulk because its flat S–C=S=O skeleton is perpendicular to the co-ordination plane.[1]

(*ii*) *The Mechanism of the* (*E*)–(*Z*) *Isomerization of* η^2-CS *Co-ordinated Platinum–Sulphine Complexes and of Platinum-substituted Sulphines.*—Although the η^2-CS co-ordinated platinum–sulphine complexes could be made with retention of configuration of the sulphine skeleton, in case of the PPh_3 complexes isomerization of the sulphine occurred upon oxidative addition of the C–S side bond.[12] For example, conversion of (*E*)-(2b) yielded not only (*E*)- but also (*Z*)-(3b), and (*Z*)-(2b) also gave rise to (*E*)-(3b) [12,13] (see Scheme). Recently, we considered three possible isomerization processes to explain this phenomenon.[12] (*a*) Isomerization in the η^3-SCS bonded intermediates [see section (*i*)]; (*b*) isomerization between the platinum-substituted sulphines (*E*)- and (*Z*)-(3b); and (*c*) dissociation of the sulphine of (*E*)- and (*Z*)-(2b), with isomerization of the free sulphines (*E*)- and (*Z*)-(1b) followed by re-co-ordination.



SCHEME R = Ph or C_6H_{11}; R' = *p*-MeC_6H_4; proposed intermediates are marked with a ‡

On the basis of the present results a choice between these three types of isomerization seems possible. The fact that isomerization between (*E*)- and (*Z*)-(5b) is concentration-independent shows that the reaction must be intramolecular. This excludes the third possibility, provided that the same isomerization mechanism is followed both for $P(C_6H_{11})_3$ and PPh_3 complexes. The second mechanism cannot be alone responsible for the isomerization, because for $P(C_6H_{11})_3$ the C–S oxidative-addition process is blocked, yet (*E*)- and (*Z*)-(5b) still isomerize. Thus, at least for $P(C_6H_{11})_3$ complexes, isomerization *via* pathway (*a*) must occur.

(*E*)–(*Z*) Isomerization [pathway (*b*)] in *cis*-(*E*) and -(*Z*)-$[Pt^{II}Cl(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]$, (*E*)- and (*Z*)-(3d), in $CDCl_3$ was not found.[1] This conclusion strongly suggests that direct isomerization between the platinum-substituted sulphine stereoisomers (*E*)- and (*Z*)-(3c) [1] [pathway (*b*)] is also unlikely. We have already seen that direct isomerization between η^2-CS co-ordination stereoisomers seems unlikely, then the isomerization between the oxidative-addition stereoisomers must also proceed *via* η^3-SCS co-ordinated intermediates, *i.e.* a reductive coupling–isomerization–oxidative-addition process.

The η^3-SCS co-ordinated platinum–sulphine complexes $[Pt^0(PR_3)_2\{(E)\text{-}MeSC(R')SO\}]$, $[Pt^0(PR_3)_2\{(Z)\text{-}MeSC(R')SO\}]$, $[Pt^0(PR_3)_2\{(E)\text{-}R'SC(SR')SO\}]$, and $[Pt^{II}(PR_3)_2\{(Z)\text{-}R'SC(SR')SO\}]$ (R = C_6H_{11} or Ph; R' = *p*-MeC_6H_4) are likely to be intermediates or transition states in both the intramolecular oxidative-addition and reductive-coupling processes (R = Ph) as well as in the intramolecular (*E*)–(*Z*) isomerization processes (R = Ph or C_6H_{11}) (see Scheme).

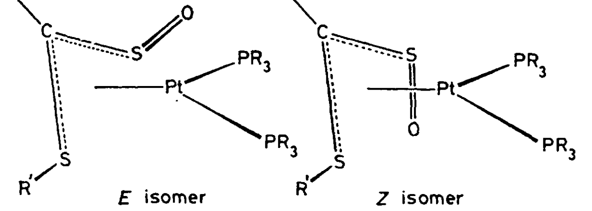


FIGURE 4 η^3-SCS co-ordinated intermediates or transition states (X = *p*-MeC_6H_4, R' = Me, R = C_6H_{11} or Ph; X = R'S, R' = *p*-MeC_6H_4, R = C_6H_{11} or Ph)

In the complexes $[Rh^ICl(PR_3)\{(E)\text{-}MeSC(R')SO\}]$ (*E*)-(8b) and -(9b), $[Rh^ICl(PR_3)\{(Z)\text{-}MeSC(R')SO\}]$ (*Z*)-(8b) and -(9b), $[Rh^ICl(PR_3)\{(E)\text{-}R'SC(SR')SO\}]$ (*E*)-(8c) and -(9c), and $[Rh^ICl(PR_3)\{(Z)\text{-}R'SC(SR')SO\}]$ (*Z*)-(8c) and

-(9c) ($R = C_6H_{11}$ or Pr^i; $R' = p$-MeC_6H_4) the sulphines are found to be co-ordinated η^3-SCS to the rhodium(I) centres. This further evidence for η^3-SCS co-ordination is to be the subject of a forthcoming paper.[18]

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REFERENCES

[1] Part 3, J. W. Gosselink, G. van Koten, A. M. F. Brouwers, and O. Overbeek, *J. Chem. Soc., Dalton Trans.*, 1981, 342.

[2] Th. W. Hummelink, *Cryst. Struct. Commun.*, 1975, **4**, 441.

[3] R. B. Bates and G. A. Wolfe, *J. Am. Chem. Soc.*, 1968, **90**, 6854.

[4] J. P. Snijder and D. N. Harpp, *J. Chem. Soc., Chem. Commun.*, 1972, 1305.

[5] B. F. Bonini, L. Lunazzi, G. Maccagnani, and G. Mazzanti, *J. Chem. Soc., Perkin Trans. 1*, 1973, 2314.

[6] J. F. King and T. Durst, *J. Am. Chem. Soc.*, 1963, **85**, 2676.

[7] A. Tangerman, Ph.D. Thesis, University of Nijmegen, 1974.

[8] R. Meij, D. J. Stufkens, and K. Vrieze, *J. Organomet. Chem.*, 1978, **144**, 239; 1978, **155**, 323; 1979, **164**, 353.

[9] K. Vrieze and G. van Koten, *Recl. Trav. Chim. Pays-Bas*, 1980, **99**, 45.

[10] Part 1, J. W. Gosselink, G. van Koten, K. Vrieze, B. Zwanenburg, and B. H. M. Lammerink, *J. Organomet. Chem.*, 1979, **179**, 411.

[11] J. W. Gosselink, G. van Koten, and K. Vrieze, Proceedings of the 21st Int. Conf. Coord. Chem., University Paul Sabatier, Toulouse, France, 1980, p. 305.

[12] Part 2, J. W. Gosselink, G. van Koten, A. L. Spek, and A. J. M. Duisenberg, *Inorg. Chem.*, 1981, in the press.

[13] J. W. Gosselink, A. M. F. Brouwers, G. van Koten, and K. Vrieze, *J. Chem. Soc., Chem. Commun.*, 1979, 1045.

[14] C. A. Tolman, *J. Am. Chem. Soc.*, 1970, **92**, 2956; *Chem. Rev.*, 1977, 313.

[15] G. E. Veenstra and B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, 1976, **95**, 28, 37, 195, 202; *Tetrahedron*, 1978, **34**, 1585.

[16] M. van der Leij, P. A. T. W. Porskamp, B. H. M. Lammerink, and B. Zwanenburg, *Tetrahedron Lett.*, 1978, 811.

[17] M. Green, J. A. Howard, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1975, 3; *J. Chem. Soc., Dalton Trans.*, 1977, 271.

[18] Part 5, J. W. Gosselink, A. M. F. Brouwers, G. van Koten, and K. Vrieze, in preparation.

[19] F. H. Allen and A. Pidcock, *J. Chem. Soc. A*, 1968, 2700.

[20] S. J. Anderson, P. L. Goggin, and R. J. Goodfellow, *J. Chem. Soc., Dalton Trans.*, 1976, 1599.

[21] A. J. Carty, *Inorg. Chem.*, 1976, **15**, 1956.

[22] S. O. Grim, R. L. Keiter, and W. McFarlane, *Inorg. Chem.*, 1967, **6**, 113.

[23] G. Socrates, *J. Inorg. Nucl. Chem.*, 1968, **31**, 1667.

[24] I. M. Blacklaws, E. A. V. Ebsworth, D. W. H. Rankin, and H. E. Robertson, *J. Chem. Soc., Dalton Trans.*, 1978, 753.

[25] P. B. Hitchcock, B. Jacobson, and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 1977, 2038.

[26] E. C. Alyea, S. A. Dias, G. Ferguson, and R. J. Restivo, *Inorg. Chem.*, 1977, **16**, 2329.

[27] H. C. Clark, M. J. Dymarski, and J. D. Oliver, *J. Organomet. Chem.*, 1978, **154**, C40.

[28] A. Immirzi and A. Musco, *Inorg. Chim. Acta*, 1977, **21**, L37; 1977, **25**, L41.

[29] G. Ferguson, P. J. Roberts, E. C Alyea, and W. Kahn, *Inorg. Chem.*, 1978, **17**, 2965.

[30] C. R. Green and R. J. Angelici, *Inorg. Chem.*, 1972, **11**, 2095.

[31] A. W. Gal, Ph.D. Thesis, University of Nijmegen, 1977.

[32] E. D. Dobrzynski and R. J. Green, *J. Organomet. Chem.*, 1974, **76**, C53.