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The Ylide Adduct $SOC_2(PPh_3)_2$ as Complex Ligand. Reaction with $[Mn_2(CO)_{10}]$ and $InCl_3$; Crystal Structures of $[(CO)_4Mn(SOC_2\{PPh_3\}_2)_2][Mn(CO)_5]$ and $(H_2C\{PPh_3\}_2)[InCl_4]_2$

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Abstract. The betain-like $SOC_2(PPh_3)_2$ (**1a**) reacts with $[Mn_2(CO)_{10}]$ in THF to produce the salt-like complex $[(CO)_4Mn(SOC_2\{PPh_3\}_2)_2][Mn(CO)_5]$ (**2**). **1a** is bonded via the sulfur atoms which are arranged in *trans* position in the octahedral environment of the manganese atom. With $InCl_3$ from CH_2Cl_2 solution the addition product $[Cl_3In(SOC_2\{PPh_3\}_2)]$ (**3**) is obtained along with the salt $(H_2C\{PPh_3\}_2)[InCl_4]_2$ (**4**), which is the result of proton abstraction from the solvent. The crystal structures of **2**·0.5THF and **4**·CH_2Cl_2 are reported. The compounds are further characterized by IR and ^{31}P NMR spectroscopy.

Keywords: Betain-like compounds; Carbodiphosphorane adducts; Crystal structures; Indium compounds; Manganese carbonyl complex

1 Introduction

The betain-like compound $SOC_2(PPh_3)_2$ (**1a**) is an adduct of COS at the carbodiphosphorane $C(PPh_3)_2$ and was first mentioned in 1966 in a short note without further characterization together with the related adducts of CO_2 (**1b**) and CS_2 (**1c**) [1]. However, the chemistry of these compounds remained unexplored until recently. X-ray analyses of **1b** and **1c** were obtained by us, and attempts were also undertaken to study their properties as potential ligands towards main group or transition metal Lewis acids. According to the soft nature of the sulfur atoms of **1c**, transition metal complexes of the type $[(CO)_4M(S_2C_2\{PPh_3\}_2)]$ (M = Cr, Mo, W) [2] and $[(CO)_4Mn(S_2C_2\{PPh_3\}_2)]^+$ [3] could be prepared in which **1c** acts as a chelating ligand. Silver salts with weakly coordinating anions gave new Ag_4^{4+} and Ag_6^{6+} units which were hold together by several molecules of **1c** [4]. In contrast, the harder oxygen atoms in **1b** predestinates this adduct to join to main group fragments, and complexes could be isolated in which **1b** is present as a chelating or a monodentate ligand [5]. But also tungsten carbonyl complexes could be prepared in which **1b** acts in both manners [6]. The S and the O atoms in **1a** represent soft and hard sites of the molecule, respectively, and we were interested to explore which site could be activated if different kinds of Lewis acids are offered. Herein we report on the preparation and some properties of **1a** and the outcome of its reaction with $[Mn_2(CO)_{10}]$ and with $InCl_3$.

2 Results and Discussion

We could obtain the "mesomeric inner salt" **1a** as a colorless precipitate by bubbling gaseous COS dried over P_2O_5 into a solution of $C(PPh_3)_2$ in toluene. The IR spectrum of **1a** exhibits strong bands at 1122 and 1454 cm^{-1} according to the ν(CS) and ν(CO) vibrations, respectively. **1a** is insoluble in toluene and THF but dissolves in halogenated hydrocarbons and DMSO. A freshly prepared solution of **1a** in CH_2Cl_2 exhibits a singlet at 11.9 ppm; however, on standing for several hours it disappears in favor of the signal of the cation $(HC(PPh_3)_2)^+$, indicative for the abstraction of a proton from the solvent. This H^+ abstraction should generate either the anion $(HCCl_2)^-$ or, after release of Cl^-, the carbene HCCl. From the remaining solution of **1a** in CH_2Cl_2 we could identify small amounts of *trans*-HClC=CClH by GC/MS experiments, being the dimerization product of the postulated carbene; thus, the overall reaction can be expressed by the equations (1) and (2):

$$\mathbf{1a} + CH_2Cl_2 \rightarrow (HC\{PPh_3\}_2)Cl + COS + \text{“HCCl”} \qquad (1)$$

$$2\,\text{„HCCl”} \rightarrow trans\text{-}HClC{=}CClH \qquad (2)$$

Although the cation $(HC(PPh_3)_2)^+$ bears a free pair of electrons, no addition compound with COS similar to that with Ag^+ is found [7]; however, a further protonation to give the dication is possible as shown below.

Addition of **1a** to a solution of $[Mn_2(CO)_{10}]$ in THF yields a suspension, and after stirring the mixture magnetically for some hours all material has dissolved to give an orange yellow solution. Layering the solution with *n*-pentane produced small yellow crystals along with larger pale orange crystals. Whereas the yellow crystals could not be identified as yet, the orange ones were found to be the salt-

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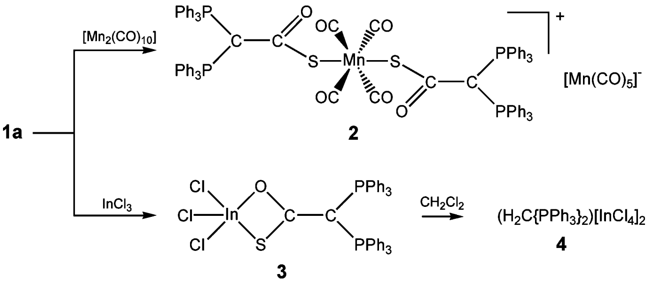

Scheme 1

like complex $[(CO)_4Mn(SOC_2\{PPh_3\}_2)_2][Mn(CO)_5]$ (**2**) as depicted in Scheme 1.

The formation of **2** can be explained with a ligand induced heterolytic cleavage of $[Mn_2(CO)_{10}]$ in THF into the cation $[Mn(CO)_5]^+$ and the anion $[Mn(CO)_5]^-$. The electron deficient cation is very reactive and gains stability under addition of two molecules of **1a** and release of CO. One can also speculate on a stepwise substitution via the $[(CO)_5Mn(SOC_2\{PPh_3\}_2)]^+$ cation as intermediate and subsequent CO/**1a** exchange. The ^{31}P NMR spectrum of **2** in THF or CH_2Cl_2 exhibits a singlet at 18.0 ppm, thus inducing a low field shift of **1a** upon complex formation. The IR spectrum of **2** in the ν(CO) region is composed of clearly separated bands of anion and cation. The low frequency bands at 1854, 1885, and 1902 cm^{-1} can be assigned to the vibrations of the CO groups of the anion (A_2'', E'); this band pattern (with splitting of the E' mode) is typical for the anion according to a deviation from the ideal D_{3h} symmetry [2, 8]. Further two bands at 1939 and 1973 cm^{-1} belong to the vibrations of the four CO groups of the cation. For a local D_{4h} symmetry only the IR active E_u band is expected [9] but the ligands **1a** apparently cause the degeneracy to be cancelled. One strong band at 1084 cm^{-1} can be assigned to the ν(C=S) and a medium strong band at 1530 cm^{-1} to the ν(C=O) vibrations of the ligand; the shift of the ν(C=O) band to higher frequencies upon complex formation is due to an increase of double bond character.

The soft-soft coordination in **2** prompted us to examine the possibility of a related hard-hard coordination via the oxygen atom of **1a**. For this reason we chose $InCl_3$ as a Lewis acid and the reaction was performed in CH_2Cl_2 solution. Immediately after starting the reaction, the ^{31}P NMR spectrum showed a signal at 11.7 of unreacted **1a**, two intense signals at 20.1 and 20.6 ppm, and two less intense signals at 20.9 and 21.2 ppm, indicating the formation of different reaction products. After about 2 h an intense singlet at 20.6 ppm and a less intense one at 20.9 ppm remained in the ^{31}P NMR spectrum of the clear colorless solution; after 24 h the signal at 20.9 ppm has disappeared. Precipitation with *n*-pentane gave a colorless powder. Attempts to grow crystals for an X-ray analysis produced two sorts of crystals upon layering a methylene chloride solution with *n*-pentane. Some crystals of bad quality turned out to be the addition compound $[Cl_3In(SOC_2\{PPh_3\}_2)]$ (**3**), in which **1a** acts as a chelating ligand with the indium atom in a trigonal bipyramidal environment similar as in the reaction product of $InCl_3$ with $O_2C_2(PPh_3)_2$ (**1b**) as depicted in Scheme 1 [5].

Apparently $InCl_3$ is not “hard” enough to avoid an S coordination; a chelating effect may also be taken into account. The majority of crystals of sufficient quality, however, turned out to be the salt $(H_2C\{PPh_3\}_2)[InCl_4]_2$ (**4**) as a result of solvent deprotonation according to equ. (1) but with formation of the dication. On longer standing of the solution only crystals of $\mathbf{4}\cdot CH_2Cl_2$ could be isolated. Why the presence of $InCl_3$ favors the formation of the dication instead of the salt $(HC\{PPh_3\}_2)[InCl_4]$ is not yet clear. The signal at 20.2 ppm in the ^{31}P NMR spectrum is due to the cation of **4** but it is close to that of the monocation $(HC(PPh_3)_2)^+$. Addition of $(HC(PPh_3)_2)I$ to the CH_2Cl_2 solution of **4** produces a separate signal at 21.1 ppm due to this cation.

The salt-like compound **4** is one of the rare examples with the dication $(H_2C\{PPh_3\}_2)^{2+}$ established by X-ray analysis [7, 10]; the salt $(H_2C\{PPh_3\}_2)Br_2$ described earlier was used as starting material for the preparation of the carbodiphosphorane $C(PPh_3)_2$ [11]. However, none of the known salts with the dication $(H_2C\{PPh_3\}_2)^{2+}$ was obtained from double protonation of $C(PPh_3)_2$.

3 Crystal Structures

To get more insight into the nature of the complexes and the bonding situation, X-ray analyses of the compounds were performed. Pale orange crystals of the salt $\mathbf{2}\cdot 0.5THF$ suitable for an X-ray analysis formed upon layering a THF solution of the reaction mixture at room temperature with *n*-pentane. The compound was refined as a racemic twin with 0.43(3):0.57(3). Colorless crystals of **3** and $\mathbf{4}\cdot CH_2Cl_2$ were obtained by layering a CH_2Cl_2 solution of the reaction mixture with *n*-pentane. However, the bad diffraction quality of the crystals of **3** did not allow to obtain satisfactory R values and only a low-resolution solution of the structure could be determined. The crystal structure of the dication $(H_2C\{PPh_3\}_2)^{2+}$ was first described as the $[FeCl_4]^-$ salt, but this compound was obtained from interaction of $FeCl_3$ with PPh_3 in $CHCl_3$ solution [10]. The structures of the cation of $\mathbf{2}\cdot 0.5THF$ and of $\mathbf{4}\cdot CH_2Cl_2$ are shown in Figure 1 and 2, respectively; crystallographic data are collected in Table 1; distances and angles are summarized in Tables 2 and 3.

3.1 Crystal Structure of $\mathbf{2}\cdot 0.5THF$

The compound **2** represents the first complex with a cationic $(CO)_4MnS_2$ core in which the sulfur atoms are in a *trans* arrangement. The cation of the salt-like complex contains two molecules of **1a** which coordinate with the sulfur atoms at the manganese atom in an η^1 manner. The manganese atom is in an octahedral environment with a planar $Mn(CO)_4$ array. The C-Mn-C angles are slightly different from 90° showing a pair of smaller and a pair of larger ones. The distances between the manganese atom and the

Table 1 Crystal data and structural refinement details

	$\mathbf{2} \cdot 0.5THF$	$\mathbf{4} \cdot CH_2Cl_2$
Formula	$C_{87}H_{64}Mn_2O_{11.5}P_4S_2$	$C_{38}H_{34}Cl_{10}In_2P_2$
$mw/g \cdot mol^{-1}$	1591.34	1136.81
a/pm	988.0(1)	1124.0(1)
b/pm	3101.4(2)	1213.2(2)
c/pm	1318.0(1)	1851.4(2)
α/deg	90	105.48(1)
β/deg	97.08(1)	106.79(1)
γ/deg	90	94.96(1)
crystal size/mm	0.18×0.15×0.07	0.19×0.05×0.05
$volume/pm^3$	$4007.8(6) \times 10^6$	2292.4(5)
Z	2	2
d_{calc} $/g \cdot cm^{-3}$	1.319	1.647
crystal system	monoclinic	triclinic
space group	$P2_1$ (Nr. 4)	$P\bar{1}$ (Nr. 2)
diffractometer	IPDS II (Stoe)	IPDS II (Stoe)
radiation	Mo-K_α	Mo-K_α
temp/K	193	100
μ/cm^{-1}	5.1	16.9
$2\theta_{max}$/deg	52.47	52.04
index range	$-12 \leq h \leq 12$	$-13 \leq h \leq 13$
	$-36 \leq k \leq 38$	$-14 \leq k \leq 14$
	$-14 \leq l \leq 16$	$-22 \leq l \leq 22$
No. of rflns collected	30374	29110
No. of indep. rflns (R_{int})	14102 (0.1088)	8921 (0.0812)
No. of observed rflns with $F_0 > 4\sigma(F_0)$	7028	4717
parameters	944	478
absorption correction	numerical	numerical
structure solution	direct methods SHELXS-97 [18]	direct methods SHELXS-97 [18]
refinement against F^2	SHELXL-97 [19]	SHELXL-97 [19]
H atoms	calculated positions with common displacement parameter	calculated positions with common displacement parameter. H(1) and H(2) were refined free
R_1	0.0683	0.0368
wR_2 (all data)	0.1512	0.0633
max. electron density left $(e/pm^3) \times 10^{-6}$	0.44	0.58

carbonyl carbon atoms range between 181 and 189 pm. The cation is centrosymmetric (not crystallographically) as depicted in Figure 1. The C-C bond lengths in the ligands are 148 and 147 pm, and the dihedral angles SOC/P_2C amount to 18° and 20°, respectively; both parameters are probably due to a π interaction of the filled p orbital at the PCP carbon atom with the vacant p orbital of the OCS carbon atom. The atoms C(6) and C(44) are in a planar environment with the sum of the angles of 359.8(7)° and 359.9(7)°. The Mn-S distances are normal as found in other compounds with the $(CO)_4MnS_2$ units [12], but shorter than in compounds with a $(CO)_5MnS$ moiety [13]. The two C-S bond lengths differ by about 5 pm, but are longer than the mean value of C-S distances of about 170 pm in the free ligand $S_2C_2(PPh_3)_2$ (**1c**) and in its $(CO)_4M$ complexes (M = Cr, Mo, W [2], Mn^+ [3]) indicating only a weak double bond character. In contrast, the uncoordinated C-O bonds differ by about 4 pm but are closely related to those in the η^1 bonded ligand $O_2C_2(PPh_3)_2$ (**1b**). It is interesting to see that in **2** the long C-S bond belongs to the short C-O bond while the short C-S bond is accompanied by the long C-O bond. The anion shows a slight disorder but the parameters are closely related to those in other complexes with this anion [8].

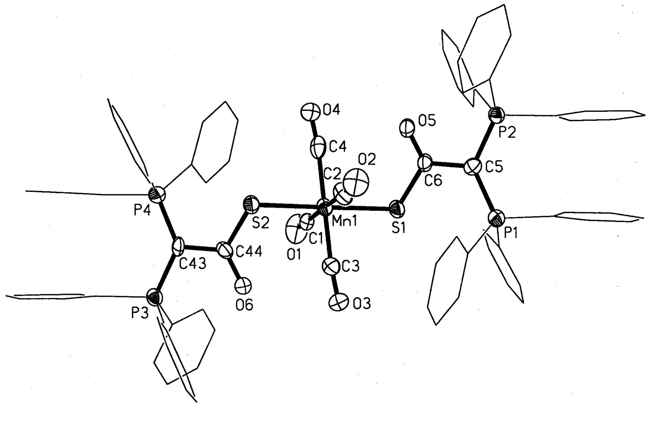

Fig. 1 Molecular structure of the cation of $[(CO)_4Mn(SOC_2\{PPh_3\}_2)_2][Mn(CO)_5]$ ($\mathbf{2} \cdot 0.5THF$) showing the atom numbering scheme. The ellipsoids are drawn at a 40 % probability level; the H atoms at the phenyl rings are omitted for clarity.

3.2 Crystal Structure of $\mathbf{4} \cdot \mathbf{CH_2Cl_2}$

The molecular structure of $\mathbf{4} \cdot CH_2Cl_2$ is shown in Figure 2. The CH_2Cl_2 molecules are disordered and not shown. The P-C-P angle amounts to 123° and is more acute than the

Table 2 Selected bond lengths/pm and angles/° in the cation of **2**

Mn(1)−S(1)	236.8(3)	Mn(1)−S(2)	236.4(3)
Mn(1)−C(1)	187 (1)	Mn(1)−C(2)	181 (1)
Mn(1)−C(3)	185 (1)	Mn(1)−C(4)	189(1)
S(1)−C(6)	178.2(9)	S(2)−C(44)	173.4(8)
P(1)−C(5)	175.3(9)	P(3)−C(43)	175.1(8)
P(2)−C(5)	173.3(8)	P(4)−C(43)	175.4(9)
O(1)−C(1)	110(1)	O(2)−C(2)	119(1)
O(3)−C(3)	112(1)	O(4)−C(4)	114(1)
O(5)−C(6)	122(1)	O(6)−C(44)	126(1)
C(5)−C(6)	148(1)	C(43)−C(44)	147(1)
S(1)−Mn(1)−S(2)	179.6(1)	S(1)−Mn(1)−C(1)	90.8(3)
S(1)−Mn(1)−C(2)	90.0(3)	S(1)−Mn(1)−C(3)	85.3(3)
S(1)−Mn(1)−C(4)	94.9(3)	S(2)−Mn(1)−C(1)	89.0(3)
S(2)−Mn(1)−C(2)	90.1(3)	S(2)−Mn(1)−C(3)	95.1(3)
S(2)−Mn(1)−C(4)	84.7(3)	C(1)−Mn(1)−C(2)	177.7(5)
C(1)−Mn(1)−C(3)	87.0(4)	C(1)−Mn(1)−C(4)	93.4(4)
C(2)−Mn(1)−C(3)	91.0(5)	C(2)−Mn(1)−C(4)	88.7(4)
C(3)−Mn(1)−C(4)	179.6(4)	Mn(1)−S(1)−C(6)	108.6(3)
Mn(1)−S(2)−C(44)	110.0(3)	C(5)−P(1)−C(7)	111.6(4)
C(5)−P(1)−C(13)	115.1(4)	C(5)−P(1)−C(19)	112.4(4)
C(5)−P(2)−C(31)	114.1(4)	C(5)−P(2)−C(25)	115.7(4)
C(43)−P(3)−C(51)	114.7(4)	C(5)−P(2)−C(37)	108.5(4)
C(43)−P(3)−C(57)	113.9(4)	C(43)−P(3)−C(45)	108.0(4)
C(43)−P(4)−C(63)	114.7(4)	C(43)−P(4)−C(69)	104.9(4)
C(43)−P(4)−C(75)	113.9(4)	Mn(1)−C(1)−O(1)	178.1(9)
Mn(1)−C(2)−O(2)	176.3(9)	Mn(1)−C(3)−O(3)	174.0(8)
Mn(1)−C(4)−O(4)	174.3(8)	P(1)−C(5)−P(2)	130.6(5)
P(1)−C(5)−C(6)	119.4(6)	P(2)−C(5)−C(6)	109.8(6)
S(1)−C(6)−O(5)	122.6(7)	S(1)−C(6)−C(5)	116.0(6)
O(5)−C(6)−C(5)	121.2(8)	P(3)−C(43)−P(4)	130.6(5)
P(3)−C(43)−C(44)	111.0(6)	P(4)−C(43)−C(44)	118.4(6)
S(2)−C(44)−O(6)	123.0(7)	S(2)−C(44)−C(43)	118.2(6)
O(6)−C(44)−C(43)	118.7(7)		

related angle in $(HC\{PPh_3\}_2)^+$ (130°). The carbon atom of the CH_2 group is in a distorted tetrahedral environment with an approximate sp^3 hybridization and the deviation of the P-C-P angle from a normal tetrahedral angle presumably is a result of the bulkiness of the PPh_3 groups. Each H atom forms a weak H bridge to an $[InCl_4]^-$ anion with C(1)····Cl distances of 360 and 403 pm to Cl(5) and Cl(4), respectively. The C-H distances in the CH_2 group are significantly longer than the C-H distance in the monocation $(HC\{PPh_3\}_2)^+$. The P-C bond lengths to C(1) are very long (182.5(5) ppm) but they are in the expected range for an sp^3 carbon atom in a P-C single bond; shorter bond lengths are found in the monocation (169.9(2) pm) and in the carbodiphosphorane (163.5(5) pm); these bond shortenings are due to a partial back bonding of the occupied p orbitals at the carbon atom into σ* P-C_{phenyl} orbitals. The $[InCl_4]^-$ anions display fairly regular tetrahedrons. The In-Cl bond lengths vary between 232.8(2) and 236.5(2) pm (average 234.4(2) pm) and can be compared with those found in other salts containing this anion [14].

4 Conclusion

The hexaphenylcarbodiphosphorane adduct **1a** is soluble in CH_2Cl_2 but reacts slowly with the solvent to give the cation $(HC\{PPh_3\}_2)^+$. This is also the case for the related CO_2 adduct **1b** and both are able to act as monodentate or bidentate ligand. However, the related CS_2 adduct **1c** was only observed in an η^2 bonding manner to transition metals [4]. From earlier results we know that **1b** in the presence of Lewis acids form either complexes or deprotonate solvents like dichloromethane or even THF more quickly with result of the cations $(HC\{PPh_3\}_2)^+$ or $(H_2C\{PPh_3\}_2)^{2+}$ [15]. As yet, we are not able to predict what cation will be formed, and the outcome probably depends on the nature of the solvent and the Lewis acid attached. The formation of the compounds **2**, **3** and **4** as well as the reaction with CH_2Cl_2 demonstrates that **1a** acts in the same manner.

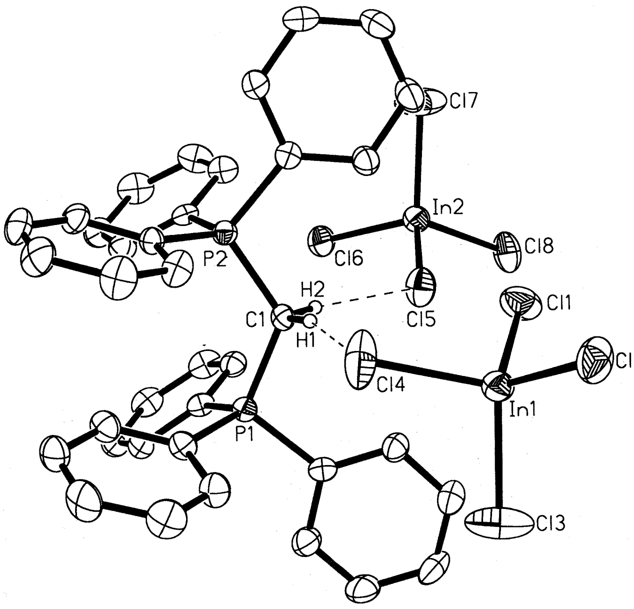

Fig. 2 Molecular structure of $(H_2C\{PPh_3\}_2)[InCl_4]_2$ ($\mathbf{4}\cdot CH_2Cl_2$) showing the atom numbering scheme. The ellipsoids are drawn at a 40 % probability level; the H atoms at the phenyl rings are omitted for clarity.

Table 3 Selected bond lengths/pm and angles/° in $\mathbf{4}\cdot CH_2Cl_2$

P(1)−C(1)	182.5(5)	P(1)−C(2)	178.5(5)
P(1)−C(8)	179.1(4)	P(1)−C(14)	179.3(5)
P(2)−C(1)	182.5(5)	P(2)−C(20)	179.1(5)
P(2)−C(26)	178.3(4)	P(2)−C(32)	179.9(5)
C(1)−H(1)	97(3)	C(1)−H(2)	92(4)
In(1)−Cl(1)	236.5(2)	In(1)−Cl(2)	232.8(1)
In(1)−Cl(3)	232.8(2)	In(1)−Cl(4)	235.3(2)
In(2)−Cl(5)	236.2(1)	In(2)−Cl(5)	233.5(1)
In(2)−Cl(5)	234.0(2)	In(2)−Cl(5)	234.3(2)
C(1)−P(1)−C(2)	110.0(2)	C(1)−P(1)−C(8)	110.9(2)
C(1)−P(1)−C(14)	109.5(2)	C(1)−P(2)−C(26)	110.6 (2)
C(1)−P(2)−C(20)	106.1(2)	C(1)−P(2)−C(32)	110.8(2)
P(1)−C(1)−P(2)	123.1(3)	P(1)−C(1)−H(1)	108(2)
P(1)−C(1)−H(1)	104(2)	P(2)−C(1)−H(1)	105(2)
P(2)−C(1)−H(2)	105(2)	H(1)−C(1)−H(2)	110(3)
Cl(1)−In(1)−Cl(2)	111.97(6)	Cl(1)−In(1)−Cl(3)	111.92(6)
Cl(1)−In(1)−Cl(4)	105.94(6)	Cl(2)−In(1)−Cl(3)	110.66(6)
Cl(2)−In(1)−Cl(4)	110.91(6)	Cl(3)−In(1)−Cl(4)	105.12(8)
Cl(5)−In(2)−Cl(6)	111.36(5)	Cl(5)−In(2)−Cl(7)	108.59(6)
Cl(5)−In(2)−Cl(8)	107.72(6)	Cl(6)−In(2)−Cl(7)	109.62(6)
Cl(6)−In(2)−Cl(8)	108.65(5)	Cl(7)−In(2)−Cl(8)	112.87(7)

Unfortunately we could not obtain the crystal structures of the potential O,S ligand **1a** or of **3** as yet in order to compare the parameters of **1a** in different bonding modes.

However, as reported earlier, data for the related O,O ligand **1b** are available. If we compare the C-C bond length in **1b** (149.4(3) pm) with those in the complexes $[(CO)_4W\{O_2C_2\{PPh_3\}_2]$ (η^2), $[(CO)_5W\{O(O)C_2\{PPh_3\}_2]$ (η^1) [6] and $[Cl_2Sn\{O(O)C_2\{PPh_3\}_2]$ (η^1) [5], amounting to 144.4(9), 147.5(8) and 145.3(8) pm, respectively, it can be deduced that the double bond character of the C-C bond in the ligand systems **1b** increases in the row **1b** < η^1-**1b** < η^2-**1b** corresponding to an electron release caused by the Lewis acids which is compensated by a stronger π donation from the filled p orbital of the ylidic carbon atom to the empty p orbital of the heteroallene carbon atom. The C-C bond length in **2** is 148(1) pm and close to the value in the η^1 bonded tungsten complex $[(CO)_5W\{O(O)C_2\{PPh_3\}_2]$ indicating a similar electron release.

The isolation of **2** and **3** demonstrates the ability of **1a** to act as monodentate or chelating ligand, but the question of donating exclusively with the O-site is still open. Further studies on the complex chemical properties of **1a** are in progress and concentrate on the choice of suitable hard Lewis acids and on finding conditions to minimize solvent reactions by sufficient solubility properties.

5 Experimental Section

All operations were carried out under an argon atmosphere in dried and degassed solvents using Schlenk techniques. The solvents were thoroughly dried and freshly distilled prior to use. The IR spectra were run on a Nicolet 510 spectrometer. For the ^{31}P NMR spectra we used the instrument Bruker AC 200. **1a** was prepared according to a modified literature procedure [1]; COS was obtained as described in [16]. Commercially available $[Mn_2(CO)_{10}]$ was sublimed prior to use, and $InCl_3$ was obtained according to literature procedures from the elements [17].

Preparation of $SOC_2(PPh_3)_2$ (1a): Freshly prepared COS gas was introduced into a solution of 2.81 g $C(PPh_3)_2$ (5.2 mmol) in toluene [1]. A pale yellow powder of **1a** precipitated quantitatively, which was filtered and dried in vacuo. **1a** is insoluble in toluene but dissolves in CH_2Cl_2 or 1,2-dichloroethane under slow decomposition and formation of the cation $(HC\{PPh_3\}_2)^+$. ^{31}P NMR (CH_2Cl_2): s, 11.9 ppm. IR (Nujol mull, cm^{-1}): 1586 w, 1568 w, 1483 s, 1454 vs, 1437 s, 1358 w, 1312 w, 1184 w, 1161 w, 1154 w, 1123 vs, 1099 vs, 1026 w, 999 m, 745 m, 718 m, 706 m, 691 s, 588 m, 534 m, 521 s.

Reaction of 1a with some solvents: A solution of 100 mg of **1a** was dissolved in 2 mL of CH_2Cl_2. The ^{31}P NMR spectrum showed singlets at 11.9 ppm and 20.6 ppm in a 1:0.3 ratio immediately after dissolving assigned to **1a** and the cation $(HC\{PPh_3\}_2)^+$, respectively. After about 3 h only the signal of the cation was found. The solution was allowed to stand for about 10 h; then all volatile material was distilled off and collected. The mixture was separated by GC/MS; from MS studies the formation of *trans*-HClC=CClH could be established. If **1a** was dissolved in 1,2-dichloroethane solution similarly the formation of the cation was observed. In DMSO solution a singlet appeared at 10.0 ppm, which did not change within 24 h. The compound is insoluble in THF and toluene.

Preparation of $[(CO)_4Mn(SOC_2\{PPh_3\}_2)_2][Mn(CO)_5]$ (2): To a suspension of 0.148 g of **1a** (2.48 mmol) in about 10 ml THF was added 0.100 g $[Mn_2(CO)_{10}]$ (2.50 mmol) and the mixture was stirred magnetically for about 48 h. The resulting orange solution was filtered from small amounts of an insoluble material and layered with *n*-pentane. After 2 days orange crystals have separated along with some small yellow crystals. The orange crystals were separated and identified as **2**·0.5THF. ^{31}P NMR (CH_2Cl_2): s, 18.0 ppm. IR (Nujol mull, cm^{-1}): 1973 s, 1939 s, 1902 s, 1885 m, 1854 vs, 1588 w, 1530 m, 1483 m, 1441 s, 1402 w, 1261 w, 1103 vs, 1084 sh, 1028 w, 999 w, 745 m, 719 m, 683 m, 658 w, 650 w, 619 w, 583 w.

Reaction of 1a with $InCl_3$: 510 mg of **1a** (0.86 mmol) and 190 mg $InCl_3$ (0.86 mmol) were dissolved in about 20 ml CH_2Cl_2 at 0 °C and the mixture was stirred for 20 min. A clear solution was obtained. In the ^{31}P NMR spectrum of the solution after about 20 min two signals at 20.1 and 20.6 ppm were found attributed to **3** and **4**, respectively. The mixture was allowed to stand for about 5 h at room temperature. Then it was layered with *n*-pentane. After several days crystals separated which consisted mainly of **4**. IR (Nujol mull, cm^{-1}): 1481 m, 1439 s, 1337 w, 1316 w, 1265 w, 1169 s, 1103 vs, 1059 m, 1026 w, 997 m, 748 s, 719 m, 714 m, 691 s, 662 w, 592 w, 526 m, 517 s, 507 s.

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ. Copies of the data can be obtained on quoting the depository numbers CCDC 651194 (**2**), and CCDC 612360 (**4**), (Fax: (+44)1223-336-033; E-mail: **deposit@ccdc.cam.ac.uk**).

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