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Note

Reactions of $Cp'(CO)_2MnPPh_2H$ with CH_3COCl and $CH_3S(O)_2Cl$ in THF/triethylamine: evidence of the first complex stabilization of a phosphorus homolog of the sulfonamides

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Abstract

The complex $Cp'Mn(CO)_3$ ($Cp' = \eta^5$-C_5H_4–CH_3) reacts with $P(C_6H_5)_2H$ in THF to give $Cp'(CO)_2MnPPh_2H$ (Ph = phenyl) (**1**), by substitution of one CO ligand. The reaction of **1** with CH_3COCl and $CH_3S(O)_2Cl$ in the presence of triethylamine occurs under electrophilic substitution on the diphenylphosphane ligand yielding the acetyl and sulfonylphosphane complexes of manganese(I) $Cp'(CO)_2MnPPh_2COCH_3$ (**2**) and $Cp'(CO)_2MnPPh_2S(O)_2CH_3$ (**3**). The complex stabilization of these molecules, which are hitherto unknown in the free state, is only accomplished by blocking the free electron pair on phosphorus by coordination. The new complexes **1**, **2** and **3** were analyzed by IR, ^1H and ^{31}P NMR spectroscopy and their similar structures are discussed. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Organic unstable or reactive molecules can be stabilized through the formation of transition metal complexes, a procedure of wide application in inorganic synthesis. Classical examples are π-complexes of $Fe(CO)_3$ with cyclobutadiene, trimethylenemethane, cyclopentadienone and other similar species [1–3]. These molecules cannot be isolated under normal conditions because of their ability to undergo internal rearrangement in the free state [4,5]. Besides their actuation as organometallic complexes forming ligands, these stabilized molecules generally maintain their individuality in the complex, for example, cyclobutadiene, in $Fe(CO)_3(C_4H_4)$. This makes it possible to study their properties [1].

Belonging to this class of molecules, along with several phosphanes bonded to acyl groups (acylphosphanes), are the sulfinyl and the sulfonylphosphanes. Contrary to their homolog, the sulfinamides and sulfonamides, these species were hitherto unknown. Many synthesis attempts failed [6–8], probably due to intramolecular redox reactions of the Arbusov–Michaelis type [9,10]. Results obtained by Lorenz et al. [11,12] proved that these molecules can actuate as ligands in organometallic complexes, which leads to their stabilization.

The synthesis of phosphorus and phosphoryl compounds analogous to the sulfonamides of the type $R(O)_2SPR'_2$ and $R(O)_2SP(O)R'_2$ was attempted [13] by the reaction of the phosphinyl chlorides $R'_2P(O)Cl$ ($R' = CH_3$, C_6H_5) with silver sulfinates RSO_2Ag ($R = CH_3$, p-$CH_3C_6H_4$). Sulfinyl phosphinates $RS(O)OP(O)R'_2$, isomers from the desired sulfonylphosphane oxide, were spectroscopically detected in the reaction product; nevertheless, only the anhydrides of

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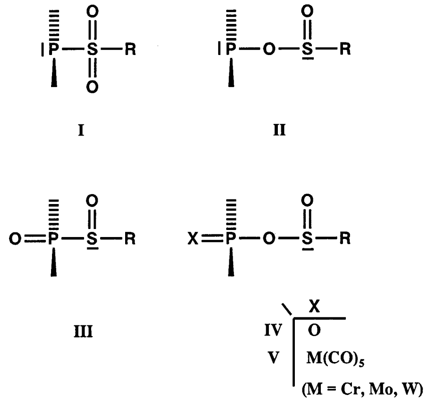


Scheme 1.

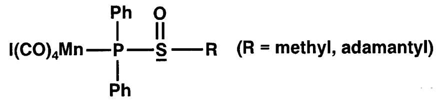
the phosphinic and sulfinic acids, respectively $[R'_2P(O)]_2O$ and $[RS(O)]_2O$, could be isolated.

These results were the basis for new attempts [11] to fix the extremely unstable sulfinylphosphinites (type **V**, Scheme 1) in the coordination sphere of a complexed metal atom, by the reactions of $(CO)_5M[P(C_6H_5)_2H]$ (M = Cr, Mo, W) with the organylsulfonyl chlorides RSO_2Cl ($R = CH_3$, p-$CH_3C_6H_4$) in triethylamine.

Stabilized type **II** isomers of sulfonylphosphane (type **I**) were also expected. However it has been verified experimentally that the sulfinylphosphinite complex appears only as an intermediary product, the decomposition of which leads to a diphosphoxane complex and sulfinylsulfone (Scheme 2).

Although the attempt had not been successful, the reaction makes possible the preparation of diphosphoxane complexes in only one step, a procedure unknown until now. Analog compounds of phosphor(V) in the form of the unstable sulfinylphosphane oxide and sulfinylphosphinates (types **III** and **IV**, respectively, Scheme 1) were detected by the same group [13,14].

The first results which signaled the real possibility that occurrence of these stabilizations were obtained as a result of reactions between the complex $I(CO)_4MnPPh_2SiMe_3$ (Ph = phenyl; Me = methyl) [15] and derivatives of the carboxylic and sulfinic acids, respectively $(CF_3CO)_2O$ and $RS(O)Cl$ (R = methyl, adamantyl), in toluene at room temperature (r.t.) [12]. The first reaction led to $I(CO)_4MnPPh_2COCF_3$, an air-unstable complex with good solubility in polar solvents. From the reaction with methyl(adamantyl)sulfinyl chloride the following products were isolated:



$$I(CO)_4Mn{-}PPh_2{-}S(O){-}R \quad (R = \text{methyl, adamantyl})$$

In this case, the occurrence of parallel reactions led to a mixture of complexes, and the compounds above could only be isolated by means of column chromatography, but in insufficient amounts for a detailed spectroscopic investigation.

These results inspired our new attempts to make feasible the stabilization of the species

(R = CH_3)

$$IPPh_2{-}C(O){-}R \qquad IPPh_2{-}S(O)_2{-}R$$

in the coordination sphere of the manganese atom, using new reagents in the substitution of the complexes $X(CO)_4MnPPh_2SiMe_3$ [15] (X = Cl, Br, I).

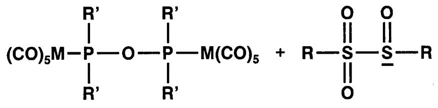
We report the synthesis and characterization by means of IR, ^1H and ^{31}P NMR of the new organometallic complexes $Cp'Mn(CO)_2PPh_2H$ (**1**), $Cp'Mn(CO)_2PPh_2COCH_3$ (**2**), and $Cp'Mn(CO)_2PPh_2S(O)_2CH_3$ (**3**) ($Cp' = \pi$-$C_5H_4CH_3$). The first was obtained by photolytic substitution of one CO ligand by the diphenylphosphane ligand in $Cp'Mn(CO)_3$ [16]. Complexes **2** and **3** were obtained by reaction of **1** with CH_3COCl (**4**) and $CH_3S(O)_2Cl$ (**5**), in the presence of triethylamine:

$$Cp'Mn(CO)_2PPh_2H + \mathbf{4},\ \mathbf{5} \underset{THF}{\overset{Et_3N}{\rightarrow}} Cp'Mn(CO)_2PPh_2L$$
$$+ Et_3NH^+Cl^-$$
$$(L = -COCH_3,\ -S(O)_2CH_3)$$

2. Experimental

All manipulations were conducted under argon by use of standard Schlenk techniques. The solvents were dried with sodium/benzophenone and distilled before use. CH_3COCl was prepared from acetic acid and PCl_3, $CH_3S(O)_2Cl$ was obtained by using the method of Hearst [17], which refluxes methanesulfonic acid with $SOCl_2$. The complex $P(C_6H_5)_2H$ was prepared by hydrolysis of $LiP(C_6H_5)_2$ [18], $Cp'Mn(CO)_3$ was obtained according to reported procedures [16,19].

IR spectra were recorded on a Brucker IFS 28 spectrophotometer, with wave number between 4000 and 400 cm^{-1}. The films (KBr windows) were prepared under argon, and measurements were made immediately after their preparation; the irradiation chamber was maintained under an argon stream a few minutes before, and during the measurements. ^1H NMR spectra were recorded on a Brucker DPX 200 spectrometer, and chemical shifts are reported relative to internal Me_4Si. The solutions in anhydrous $CDCl_3$ were prepared under argon in Schlenk tubes. ^{31}P NMR spectra were recorded on a Brucker DPX 400 spectrometer



Scheme 2.

using H_3PO_4 (85%) as the external reference. The samples were dissolved in anhydrous toluene under argon.

2.1. *(η^5-Methylcyclopentadienyl)dicarbonyl-diphenylphosphinomanganese(I), $Cp'Mn(CO)_2PHPh_2$ (**1**)*

In a 250-ml two-necked flask equipped with an argon inlet and stirring bar, 2.45 g (11.2 mmol) of $Cp'Mn(CO)_3$ was dissolved in 100 ml of THF. The yellow solution was irradiated with UV for 4.5 h under stirring at 50°C and it turned slowly red. After liberation of a stoichiometric amount of CO, 2.2 g (11.8 mmol) of diphenylphosphine was added dropwise and after 0.5 h of stirring at r.t. the mixture turned yellow. The solvent was removed under reduced pressure and the yellow-oil residue was purified by high vacuum fractionated distillation. $Cp'Mn(CO)_2PHPh_2$ separates at 90°C under a pressure of 1×10^{-3} mbar. Yield, 62% based on $Cp'Mn(CO)_3$ taken. Properties: yellow oil, air-unstable; $C_{20}H_{19}MnPO_2$ (377.284).

IR (in KBr window): ν(CO), 2017.9 s, 1912.9 s; P–H, 2285.3 (ν, m), 888.6 (δ, m); CH_3, 2975.5 (ν_{as}, m), 2903.4 (ν_s, m), 1461.3 (δ_{as}, m), 1362.9 (δ_s, m), 928.2 (δ_{as}, m); C–H, C=C Ph rings, (δ, v) 1572.5–695.5; C–H Ph rings, ($\nu_{s,as}$, v) 3100–3050 [20]; Cp–H, 3090.3 (ν, m), 1032.5 (δ, m), 830.6 (δ, m); C=C Cp ring, 1480.3 (ν, s), 1067.6 (ν, s), 669.5 (δ_{as}, m), 639.3 (δ_s, s); P–Ph, 1067.6 (ν, s). The Mn–P stretching occurs at low frequency (between 300 and 200 cm^{-1}) [21] and cannot be detected in the spectral region in which the measurements were carried out (4000–400 cm^{-1}). The IR spectrum of $Cp'Mn(CO)_3$ shows the two intensive ν(CO) bands (2025 and 1910 cm^{-1}) expected for the C_{3v} local symmetry of the $M(CO)_3$ group. No bands were observed in the region of absorption of the P–H group. ^1H NMR (200 MHz, $CDCl_3$): δ 1.95 (s, 3H, CH_3–Cp); 6.02, 4.72 (d, 1H, P–H), $J_{PH} = 260.2$ Hz, agrees with reported values for the PH coupling in compounds of phosphorus with a coordination number 4 [15,22]; 4.59, 4.55 (d, 4H, $CH_3–C_5H_4$), $^3J_{PMnCH} = 8.9$ Hz [15]; 7.5–7.2 (m, 10H, Ph groups). For the free ligand $PH(C_6H_5)_2$, δ 5.77, 4.68 (d, 1H, PH), $J_{PH} = 218.3$ Hz. ^{31}P NMR (400 MHz, toluene): 73.68–71.63 (m, PH), the two basic lines of the complex 'doublet' indicate a $J_{PH} = 331.7$ Hz, a result which is in conflict with the value for J_{PH} in the ^1H NMR measurements discussed above (260.2 Hz). Due to the reciprocity of the P–H coupling the values for J_{PH} should not be discordant in ^1H and ^{31}P NMR measurements. In the ^{31}P NMR literature J_{PH} values for tetra-coordinated phosphorus are situated between 250 and 730 Hz [12] and 254 and 330 Hz [15]. Nevertheless it is known that complexes represent special cases [22–24] with respect to the chemical shift and to the J_{PH} values. For the free ligand PPh_2H, the ^{31}P NMR spectrum shows a doublet at -39.28 and -40.60 ppm, with $J_{PH} = 214.7$ Hz.

2.2. *(η^5-Methylcyclopentadienyl)dicarbonylacetyl-diphenylphosphane–manganese(I), $Cp'Mn(CO)_2PPh_2$-$COCH_3$ (**2**)*

In a 100-ml two-necked flask equipped with an argon inlet and stirring bar, 2.07 g (5.5 mmol) of complex **1** was dissolved in 50 ml of THF. A total of 0.63 g (6.22 mmol) of triethylamine was added slowly under stirring, over a 20 min period. For 30 min 0.6 g (7.6 mmol) of acetyl chloride diluted in THF was added dropwise to the orange solution, with immediate precipitation of a large amount of a white solid (triethylammonium chloride), in an exothermic reaction. Simultaneously, the mixture turned pale yellow. The reaction was filtered and the solvent was removed under vacuum, giving a yellow–green residue which was purified by column chromatography over silica gel at -15°C, using a 2×20 cm column (eluant, toluene). One single, wide stark-orange zone contained the product. Properties: yellow–green oil, very sensitive to air; $C_{22}H_{21}MnPO_3$ (419.321).

IR (in KBr window): the basic structure of complex **1** remains unaltered, with the exception of the absorptions of the P–H group, which cannot be observed in the IR spectrum of **2**. The band at 1670.7 cm^{-1} (s) which corresponds to the stretching of the acetyl CO, and the modification of the bands corresponding to the stretchings and bendings of the methyl group are very important for the structural definition. ^1H NMR (200 MHz, $CDCl_3$): δ 1.94 (s, 3H, CH_3–Cp), 2.23, 2.20 (d, 3H, $-PPh_2COCH_3$), $^3J_{PCCH} = 6.0$ Hz, comparison with data of the free ligand is only possible with respect to the known trifluoroacetylphosphane [25], with $^3J_{PCCF} = 16$ Hz; 4.59, 4.54 (d, 4H, $CH_3–C_5H_4$). 7.69–7.17 (m, 10H, Ph groups). There was no occurrence of resonances of the PH proton. ^{31}P NMR (400 MHz, toluene): 17.69 (s, $-PPh_2COCH_3$), due to the amplitude of the ^{31}P NMR scale a signal from the $^3J_{PCCH}$ coupling, in the order of 6 Hz, should not be separated. For the complex $IMn(CO)_4PPH_2COCF_3$ of Lorenz et al. [12] the PCCF coupling was not reported, and the singlet of the phosphorus nucleus appears in the $^{31}P\{^1H\}$ NMR spectrum at $\delta = 60.2$ ppm, a value which seems to corroborate our result above.

2.3. *(η^5-Methylcyclopentadienyl)dicarbonylmethanesulfonyldiphenylphosphane–manganese(I), $Cp'Mn(CO)_2PPh_2S(O)_2CH_3$ (**3**)*

The preparation of complex **3** was carried out as above using 1.72 g (4.57 mmol) of complex **1**, 0.54 g

(5.33 mmol) of triethylamine and 0.57 g (5 mmol) of CH_3SO_2Cl. Due to the impossibility of purification by chromatography (instantaneous decomposition over the column), excess reagents cannot be added. The mixture was filtered and the solvent removed under vacuum. Complex **3** was carefully isolated from the small excess of reagents under high vacuum. A prolonged vacuum must be avoided. Properties: red oil, instantaneous decomposition in contact with air; $C_{21}H_{21}MnPO_4S$ (455.369).

IR (in KBr window): the same bands corresponding to the basic structure of complex **1** are present, with the exception of the PH bands. Modification of the bands corresponding to the stretchings and bendings of the CH_3 groups is also observed. The bands corresponding to the asymmetric and symmetric stretching of the SO_2 sulfonyl group appear at 1312.8 (m) and 1116.7 cm^{-1} (w), respectively. ^1H NMR (200 MHz, $CDCl_3$): δ 1.96 (s, 3H, CH_3–Cp); 2.35 (s, 3H, $-PPh_2S(O)_2CH_3$), the relative areas of the two singlets show a relation of 1:1. In the ^1H NMR spectrum of the sulfinyl complex $IMn(CO)_4PPh_2S(O)CH_3$ [12] only a singlet occurs for the methyl group at 2.7 ppm, also without PSCH coupling; 4.63, 4.56 (d, 4H, $CH_3-C_5H_4$), $^3J_{PMnCH} =$ 10.4 Hz; 7.50–7.18 (m, 10H, Ph rings). ^{31}P NMR (400 MHz, toluene): 32.33 (s, $-PPh_2S(O)_2CH_3$) agrees with reported δ values for sulfur compounds of phosphorus with coordination number 4 [12,22].

3. Results and discussion

Due to their physical characteristics the synthesized complexes cannot be investigated by means of X-ray diffractometry. The results of the elemental analyses are not included because of the discord between calculated and measured values, presumably as a consequence of the high instability of the compounds. The spectroscopic data discussed above allow us to conclude that the structures of **1**, **2** and **3** are probably derived from the structure of $Cp'Mn(CO)_3$: the substitution of one carbonyl for the diphenylphosphine ligand leads to the formation of **1**, whose structure is represented in Fig. 1.

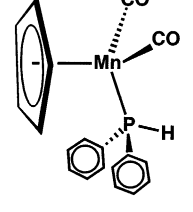
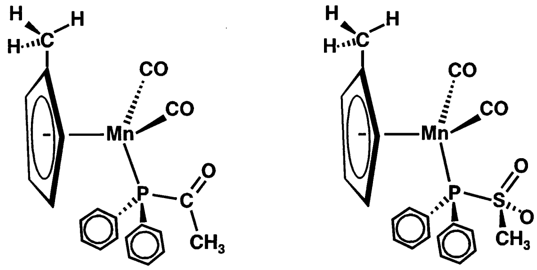


Fig. 1. Probable structure of $Cp'Mn(CO)_2PHPh_2$ (**1**).

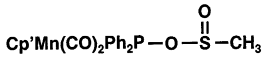


2 **3**

Fig. 2. Probable structures of $Cp'Mn(CO)_2PPh_2COCH_3$ (**2**) and $Cp'Mn(CO)_2PPh_2S(O)_2CH_3$ (**3**).

The reaction of complex **1** with CH_3COCl in the presence of triethylamine occurs simultaneously with the heterogeneous rupture of the P–H bond on the diphenylphosphine ligand and displacement of the chloride ion in CH_3COCl, under formation of the salt $Et_3NH^+Cl^-$ and complex **2**, the latter by electrophilic attack of the ion $[CH_3CO]^+$ on the ligand ion $[(C_6H_5)_2P]^-$. An identical electrophilic substitution pathway can be formulated for the reaction of **1** with $CH_3S(O)_2Cl$/triethylamine to yield **3**. IR spectra of the white solid formed during the reactions of complex **1** to give complexes **2** and **3**, were compared with the spectrum of triethylammonium chloride standard. It was confirmed that these spectra are exactly alike: in addition to the bands corresponding to the stretchings and bendings of the methyl and methylene groups, the spectra also showed the intensive bands characteristic of the R_3NH^+ vibrations of the aliphatic ammonium salts between 2760 and 2250 cm^{-1}. Fig. 2 shows the structures of **2** and **3**.

For complex **3** the formation of the sulfinylphosphinite complex analog to type **II** of Scheme 1 (sulfinylphosphinites) must also be considered:



$$Cp'Mn(CO)_2Ph_2P-O-\overset{\overset{\displaystyle O}{\|}}{S}-CH_3$$

However, due to the instability of the atomic aggregate $R_2P-O-S(O)R'$, these compounds have not yet been characterized by IR spectroscopy, and data on absorption bands of the *P–O–S(O)*R group are nonexistent. Even reports concerning absorption values for the *O–S*(O) group are rare, and the available data for the O–*S*(*O*)R group are specific for representative compounds. Nevertheless, it is possible to associate the related [20,21,26] absorptions of the S–O and O–*S*(*O*)R groups with some bands situated in the region between 1300 and 900 cm^{-1} of the IR spectrum of **3**. However, this ordination cannot be conclusive due to the wide embracing area of the reported absorption values. Finally, it must be added that **1**, **2** and **3** represent the first compounds of their classes, in which the species acetylphosphane and methanesulfonylphosphane could be stabilized as ligands on the coordination sphere of a metal atom. Analog reactions with the complex $BrMn(CO)_4PHPh_2$ led equally to compounds which should be structurally equivalent to **2** and **3**. These reactions, however, do not proceed with the same velocity and the products are extremely unstable, which indicates that the stability of the P–R bond (R = acetyl, sulfonyl) also depends on the molecular structure of the parent complex. Reactions with $Cp'Mn(CO)_2PHPh_2$ occur faster and the products are relatively more stable than those formed from the reactions with $BrMn(CO)_4PHPh_2$. This seems to reflect the stereochemical preference of complex **1** to undergo substitution reactions, possibly as a consequence of the electronic synergism of the π-Cp′–Mn bond.

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