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An Unusual Product from the Reaction of $C(PPh_3)_2$ with $[Mn_2(CO)_{10}]$: Formation and Crystal Structure of $[Mn(OPPh_3)_2\{O_2CC(PPh_3)_2\}_2][Mn(CO)_5]_2$

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Abstract. The carbodiphosphorane $C(PPh_3)_2$ (**1**) reacts with $[Mn_2(CO)_{10}]$ in THF to produce quantitatively the salt-like complex $(HC\{PPh_3\}_2)[Mn(CO)_5]$ (**2**) as THF solvate. If the reaction is carried out in 1,2-dimethoxyethane (DME) small amounts of $[Mn(OPPh_3)_2\{O_2CC(PPh_3)_2\}_2][Mn(CO)_5]_2$ (**3**) as DME solvate along with solvent free **2** as the main product were isolated. Proton abstraction from the solvent led to the formation of **2**; the ligands $OPPh_3$ and $O_2CC(PPh_3)_2\}_2$ of **3** are the results of a side reaction from $[Mn_2(CO)_{10}]$ and **1** in a Wittig type manner. From the reaction in benzene small amounts of **3** were also obtained, crystallizing as benzene solvate $\mathbf{3}\cdot 4C_6H_6$. The crystal structures of $\mathbf{2}\cdot$THF, **2**, $\mathbf{3}\cdot 1.75$DME and $\mathbf{3}\cdot 4C_6H_6$ are reported. The compounds are further characterized by IR and ^{31}P NMR spectroscopy.

Keywords: Carbodiphosphorane; Manganese complex; Proton Abstraction; Crystal Structure

1 Introduction

Many attempts have been made to study the ligand properties of the carbodiphosphorane $C(PPh_3)_2$ (**1**) towards different Lewis acids. **1** has a bent structure [1], and since the first preparation in 1961 [2], a series of addition compounds with main group [3−5] or transition metal Lewis acids [6−9] were described and characterized by crystal structure determinations. However, **1** can not be considered as a normal Lewis base with a donating pair of electrons at the carbon atom like CO, isonitriles, *N*-heterocyclic carbenes (NHC), or others, because this molecule is equipped with two occupied HOMO orbitals, which determine its chemistry, and the best description of **1** is that of a divalent carbon(0) atom stabilized by two phosphine ligands [10].

The number of transition metal carbonyl complexes of **1** is limited to two examples, although nearly all “soft” and even “hard” ligands L form complexes with 16 electron carbonyl fragments of the type $(CO)_xM\leftarrow L$. Thus, with $[Ni(CO)_4]$ the yellow complex $[(CO)_3Ni(C\{PPh_3\}_2)]$ and the red electron deficient compound $[(CO)_2Ni(C\{PPh_3\}_2)]$ could be isolated and characterized by X-ray analyses as the only established carbonyl derivatives of **1** as yet, and the outcome of the reaction depends on the choice of the solvent [9]. When we turned to $[Fe(CO)_5]$ no CO substitution was observed but a nucleophilic attack of **1** at a carbonyl carbon atom occurred to produce the heterocumulene complex $[(CO)_4Fe(CCPPh_3)]$ and $OPPh_3$ in a Wittig type manner [11]. The same was true for $[Co_2(CO)_8]$; however, only a tetranuclear cluster containing the heterocumulene ligand $CCPPh_3$ could be isolated and characterized by X-ray analysis [12]. These reactions demonstrate the hard Lewis base character of **1**. Complexes with **1** and group 6 carbonyl compounds $[M(CO)_6]$ were mentioned in the literature, but non of them was sufficiently characterized [13]. Here we report on the outcome of the reaction of **1** with $[Mn_2(CO)_{10}]$ in various solvents.

2 Results and Discussion

If **1** was allowed to react with $[Mn_2(CO)_{10}]$ in thoroughly dried THF solution, the salt $(HC\{PPh_3\}_2)[Mn(CO)_5]$ (**2**) was obtained in high yield and crystals could be identified as $\mathbf{2}\cdot$THF. The ^{31}P NMR of the THF solution showed only the signal of the cation at 20.6 ppm. The source of the proton originates from the solvent; similar results were found earlier from the reaction of $[Co_2(CO)_8]$ with **1** and a catalyzed decomposition of THF into butadiene and H_2O was suggested [12]. Thus, with $[Mn_2(CO)_{10}]$ the formation of the salt-like complex **2** was not surprising. In order to suppress proton abstraction, we switched to DME as the solvent. For this purpose DME was heated and stirred with elemental potassium and distilled prior to use to avoid any influence of humidity. A slow reaction occurred and, according to the low solubility of **1** in DME, a suspension formed, which within four days of stirring at room temperature under an atmosphere of argon produced a clear orange yellow solution. The ^{31}P NMR spectrum of this solution showed about seven singlets, indicating the formation of

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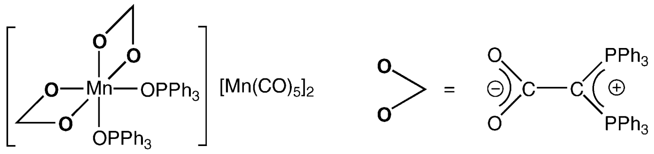
different reaction products. The most intense signal at 21.6 ppm is due to the cation $(HC\{PPh_3\}_2)^+$, which again results from proton transfer from the solvent to **1**. The signals at −10.5 and 26.0 ppm can be attributed to a compound with a MnC_2PPh_3 fragment and to Ph_3PO, respectively, probably as a result of a Wittig type reaction, but their low intensities indicate only a side reaction [11]; the signal at −3.6 ppm originates from some unreacted **1**. Layering of the DME solution with *n*-pentane produced an oil and some yellow needles, which surprisingly turned out to be the salt-like complex compound $[Mn(OPPh_3)_2\{O_2CC(PPh_3)_2\}_2][Mn(CO)_5]_2$ (**3**) as DME solvate (**3**·1.75DME), containing Mn^{II} as shown in Scheme 1. From the oil of the DME solution the solvent free salt $(HC\{PPh_3\}_2)[Mn(CO)_5]$ (**2**) could be isolated as yellow crystals. When we turned to benzene as the solvent a slow reaction was observed with formation of a yellow precipitate and an orange red oil. The ^{31}P NMR of the solution showed signals which similarly can be assigned to a Wittig type product; however, after 10 days reaction time at room temperature the signal of unreacted **1** still dominated. The oil crystallized after about two weeks and the same cation as from DME solution was isolated; the crystals were identified as **3**·$4C_6H_6$. In toluene solution the same behavior was observed.

The unusual formation of the well known ligand $O_2CC(PPh_3)_2$ as an adduct of **1** at CO_2 [14] can only be explained with a reaction of the phosphine oxide (from the Wittig reaction) with $[Mn_2(CO)_{10}]$ finally liberating CO_2 (equations (1) and (2)) which is immediately consumed by **1** according to equation (3).

$$[Mn_2(CO)_{10}] + \mathbf{1} \rightarrow \text{“}\mathbf{[Mn]}{=}C{=}C{=}PPh_3\text{”} + OPPh_3 \tag{1}$$

$$OPPh_3 + [Mn_2(CO)_{10}] \rightarrow CO_2 + [Mn_2(CO)_9(PPh_3)] \tag{2}$$

$$CO_2 + \mathbf{1} \rightarrow O_2CC(PPh_3)_2 \tag{3}$$



3

Scheme 1

The formation of Mn^{II} probably arises from disproportionation of formal Mn^0 in $[Mn_2(CO)_{10}]$ under the influence of the oxo ligands. The components of **3** can be detected in the ^{31}P NMR spectrum of the DME solution and the formation of **3** is apparently due to good crystallization properties. A weak and broad signal at 61 ppm can be assigned to $[Mn_2(CO)_9(PPh_3)]$; the ^{31}P NMR shifts of such compounds are found in this region [15]. According to the paramagnetism of **3** no signals of the complex cation were detected. A Wittig type product as supposed from ^{31}P NMR measurements could not be crystallized.

The IR spectrum of **2** shows the typical pattern of the cation; the carbonyl frequencies of the $[Mn(CO)_5]^-$ anion appear at 1900, 1860, and 1840 cm^{-1} [16]. The IR spectrum of **3** is very complex and governed by the vibrations of the aromatic systems; besides the bands of the $[Mn(CO)_5]^-$ anion also bands between 1530 and 1350 cm^{-1} were found according to ν_s and ν_{as} CO_2 vibrations of the $O_2CC(PPh_3)_2$ ligands, similar to those found in the related compounds $[Cl_3In\{O_2CC(PPh_3)_2\}]$ [17] and $[(CO)_4W\{O_2CC(PPh_3)_2\}]$ [18] in which the ligand is bonded in the same manner.

3 Crystal Structures

X-ray analyses were performed from all compounds which could be crystallized. Pale orange crystals of the salt **2**·THF suitable for an X-ray analysis formed from THF/*n*-pentane. Few yellow needles of **3**·1.75DME and big yellow blocks of the solvate free salt **2** were obtained from DME solutions as mentioned above. Yellow orange crystals of **3**·$4C_6H_6$ have grown from an orange oil, which separated from the benzene reaction mixture. The structures of **2**, **2**·THF, and of the cation of **3**·1.75DME and **3**·$4C_6H_6$ are shown in Figures 1 and 2, respectively. The crystallographic data are collected in Table 1; distances and angles are summarized in Tables 2 and 3. Further complexes with the $O_2CC(PPh_3)_2$ ligand have been reported recently coordinated at $InCl_3$ [17] and the $(CO)_4W$ fragment [18]; the structure of the free ligand was presented earlier [14].

3.1 Crystal Structures of 2 and 2·THF

The molecular structures of **2** and **2**·THF are depicted in Figure 1 (**A** and **B**). The incorporation of a solvent molecule in **2** does not markedly change the parameters of the cation $(HC\{PPh_3\}_2)^+$; the P(1)-C(6)-P(2) angle is slightly less acute in the solvent free compound. Whereas in **2** the proton of the cation forms a contact to one carbonyl oxygen atom of the anion (C(6)-H(1)·····O(1) = 341.1(2) pm) as shown in structure **A**, in **2**·THF (structure **B**) a similar contact between the proton and the oxygen atom of the THF molecule exists (C(6)-H(1)·····O(6) =345.5(5) pm); the THF molecule is disordered in two positions but only one is shown. The anion of **2**·THF forms a nearly perfect trigonal bipyramide which is slightly distorted in **2**. Other salt-like compounds of the type $(HC\{PPh_3\}_2)(X)$ were described with various counterions X [19].

3.2 Crystal Structure of 3·1.75DME

The cation of **3**·1.75DME, containing the ligands Ph_3PO and $O_2CC(PPh_3)_2$, is located on a twofold axis and the $[Mn(CO)_5]^-$ anion is disordered in two positions (0.75/0.25); the molecular structure of the cation is depicted in Figure 2. The $OPPh_3$ ligands are in a *cis* arrangement and the Mn^{2+} ion is surrounded by six oxygen atoms in a dis-

Table 1 Crystal data of complexes **2**, **2**·THF, **3**·4C_6H_6, and **3**·1.75DME

	2	**2**·THF	**3**·4C_6H_6	**3**·1.75DME
formula	$C_{42}H_{31}MnO_5P_2$	$C_{46}H_{39}MnO_6P_2$	$C_{146}H_{114}Mn_3O_{16}P_6$	$C_{129}H_{107.5}Mn_3O_{19.5}P_6$
MW	732.59	804.69	2475.01	2320.29
cryst size/mm	0.28×0.19×0.17	0.39×0.38×0.15	0.3×0.06×0.06	0.58×0.07×0.05
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	I2/a (No. 15)
a/pm	1374.6(1)	1250.9(1)	1724.6(1)	1910.7(2)
b/pm	1916.1(1)	1344.8(1)	1825.3(1)	2445.5(2)
c/pm	1386.4(1)	1455.2(1)	2229.0(1)	2735.0(4)
α/deg		62.70(1)	84.22(1)	
β/deg	90.32(1)	69.71(1)	69.39(1)	98.19(2)
γ/deg		75.46(1)	70.72(1)	
volume/pm^3	3651.5(5) × 10^6	2026.7(3) × 10^6	6290.0(6) × 10^6	12649(2) × 10^6
crystal system	monoclinic	triclinic	triclinic	monoclinic
Z	4	2	4	4
d_{calcd}	1.333	1.319	1.307	1.218
temp/K	173	193	100	193
μ/cm^{-1}	4.9	4.5	4.38	4.33
$2\theta_{max}$/deg	52.01	52.33	51.92	52.5
radiation	MoK_α	MoK_α	MoK_α	MoK_α
diffractometer	IPDS II (Stoe)	IPDS II (Stoe)	IPDS II (Stoe)	IPDS I (Stoe)
index range	$-16 \geq h \geq 16$	$-23 \geq h \geq 23$	$-21 \geq h \geq 21$	$-23 \geq h \geq 23$
	$-23 \geq k \geq 23$	$-29 \geq k \geq 30$	$-22 \geq k \geq 22$	$-29 \geq k \geq 30$
	$-17 \geq l \geq 17$	$-33 \geq l \geq 33$	$-27 \geq l \geq 27$	$-33 \geq l \geq 33$
no. of rflns collected	51014	29546	83721	62227
no. of indep rflns	7113 (R_{int} = 0.0834)	8098 (R_{int} = 0.0555)	24434 (R_{int} = 0.1351)	12480 (R_{int} = 0.2097)
no. of observed rflns	3962 ($F_0 > 4\sigma(F_0)$)	5847 ($F_0 > 4\sigma(F_0)$)	11446 ($F_0 > 4\sigma(F_0)$)	4070 ($F_0 > 4\sigma(F_0)$)
refinement against F^2	SHELXL-97 [29]	SHELXL-97 [29]	SHELXH-97 [30]	SHELXL-97 [29]
parameters	456	546	1541	706
structure solution	direct methods, SIR-92 [31]	Patterson method (SHELXTL-97-Plus [32]	direct methods, SIR-92 [31]	direct methods, SIR-92 [31]
H-atoms	calculated positions with common displacement parameter			
	H(1) was refined free			
R_1	0.0304	0.0386	0.0514	0.0586
wR_2 (all data)	0.0492	0.1032	0.0836	0.1406
max electron density left (e/pm^3) × 10^{-6}	0.27	0.39	0.629	0.458

Table 2 Selected bond lengths/pm and angles/° in **2**·THF/**2**

Mn(1)−C(1)	180.1(3)/182.3(3)	Mn(1)−C(2)	178.3(3)/178.8(2)
Mn(1)−C(3)	180.6(3)/179.6(3)	Mn(1)−C(4)	180.6(3)/179.2(3)
Mn(1)−C(5)	182.3(3)/181.5(3)	O(1)−C(1)	115.9(4)/115.3(3)
O(2)−C(2)	117.0(3)/116.8(3)	O(3)−C(3)	115.9(3)/116.6(3)
O(4)−C(4)	115.3(3)/115.3(3)	O(5)−C(5)	114.4(4)/116.3(3)
P(1)−C(6)	169.4(2)/169.3(2)	P(1)−C(7)	181.2(2)/180.3(2)
P(1)−C(13)	181.1(2)/180.4(2)	P(1)−C(19)	180.5(2)/180.8(2)
P(2)−C(6)	170.0(3)/170.3(3)	P(2)−C(25)	180.7(2)/180.8(2)
P(2)−C(31)	179.7(2)/180.9(2)	P(2)−C(37)	181.5(2)/180.8(2)
C(6)−H(1)	0.88(3)/0.83(2)		
C(6)−P(1)−C(7)	115.0(1)/113.9(1)	C(6)−P(1)−C(13)	108.0(1)/105.8(1)
C(6)−P(1)−C(19)	113.3(1)/115.9(1)	C(6)−P(2)−C(25)	110.6(1)/109.4(1)
C(6)−P(2)−C(31)	113.2(1)/113.1(1)	C(6)−P(2)−C(37)	112.3(1)/113.0(1)
P(1)−C(6)−P(2)	130.3(2)/133.8(1)	P(1)−C(6)−H(1)	115(2)/114(1)
P(2)−C(6)−H(1)	115(2)/112(1)		

torted octahedral environment with trans O-Mn-O angles of about 150° [20]. The Mn^{2+} ion belongs to two planar four-membered rings. The O(3)-Mn-(O3′) angle (97.1(2)°) is larger than that expected for an octahedral arrangement but smaller than that if we consider the Mn atom being surrounded by four ligands in an approximately tetrahedral environment. As in the benzene solvate (see below) three types of Mn-O distances are measured with distances of 208.5(3), 219.7(3), and 228.1(3) pm. The P-O bond length amounts to 149.8(4) pm, and is only slightly longer than that in the free $OPPh_3$ molecule (148.3(2) pm) [21] and in $[(Ph_3PO)_2MnCl_2]$ (148.8(6) pm) [22], but is shorter than in some $[Ph_3PO(EX_3)]$ (E = B, Al; X = F, Cl, Br) addition compounds for which a mean value of 152 pm was estimated [23, 24]. The Mn-O-P bond angle amounts to 149.2(2)° being more acute than that in $[(Ph_3PO)_2MnCl_2]$ (156.0(4)°) where the manganese atom adopts a tetrahedral environment; in Ph_3PO adducts with several main group Lewis acids related angles between 123° and 180° were found [24]. The bite angle O-C-O of the $O_2CC(PPh_3)_2$ ligand amounts to 121.3(5)°, and is slightly larger than that in $[(CO)_4W(O_2CC\{PPh_3\}_2)]$ or that in $[InCl_3(O_2CC\{PPh_3\}_2)]$, where angles of 117.6(5)° [18] and 119.6(8)° [17], respectively, were found; in the free ligand an angle of 127.7(2) was recorded [14]. The dihedral angle O_2C/CP_2 has opened to 24° from 10° in the free ligand; a similar effect was observed in other compounds with $O_2CC(PPh_3)_2$ acting as chelating ligand. The other parameters have changed only slightly upon complex formation; the C-C distance has decreased by about 1 pm whereas the C-O distances have increased in the same order [17, 18].

3.3 Crystal Structure of 3·4C_6H_6

The structural parameters of the cation have not changed markedly relative to those in the DME solvate and is therefore not depicted. Two halves of the benzene molecules are arranged around an inversion center and one of the $[Mn(CO)_5]^-$ anions is disordered. The two dihedral angles

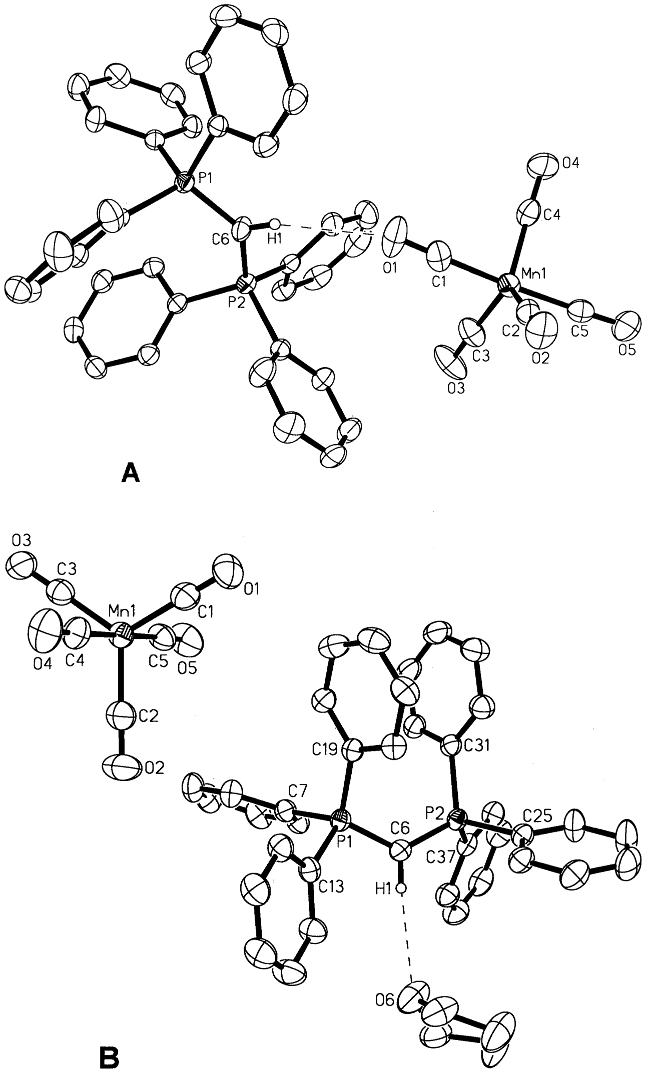


Fig. 1 Molecular structures of **2** (**A**) and **2**·THF (**B**) showing the atom numbering scheme (40 % probability for thermal ellipsoids); only one position of the disordered THF molecule is drawn; the H atoms at the phenyl rings are omitted for clarity.

O_2C/CP_2 are nearly equal amounting to 23° and 25°. Like in the DME solvate three different pairs of Mn-O distances are found. The shortest ones are the Mn-O(P) bond lengths with 208.8(2) and 210.5(2) pm; they are slightly longer than those in $[(Ph_3PO)_2MnCl_2]$ (206.9(6) pm) [24]. The Mn-O bonds to the $O_2CC(PPh_3)_2$ ligand differ by about 7 pm: the longer ones are those approximately *trans* to $OPPh_3$ with a mean value of 226.6(2) pm.

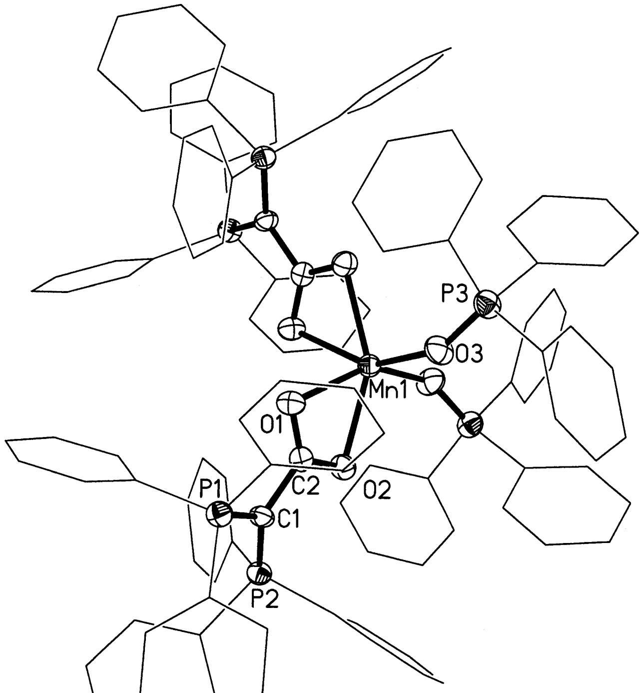


Fig. 2 Molecular structure of the cation of **3**·1.75DME showing the atom numbering scheme (40 % probability for thermal ellipsoids); the H atoms at the phenyl rings and the solvent molecules are omitted for clarity.

Table 3 Selected bond lengths/pm and angles/° in the cation of **3**·1.75DME

Mn(1)−O(3)	208.5(3)	Mn(1)−O(2)	219.7(3)
Mn(1)−O(1)	228.1(3)	Mn(1)−C(2)	257.2(5)
C(1)−C(2)	148.0(6)	C(1)−P(1)	172.3(5)
C(1)−P(2)	172.3(5)	C(2)−O(1)	126.5(5)
C(2)−O(2)	127.7(5)	O(3)−P(3)	149.8(4)
O(3)−Mn(1)−O(3′)	97.1(2)	O(3′)−Mn(1)−O(2)	91.1(1)
O(3)−Mn(1)−O(2)	107.6(1)	O(3′)−Mn(1)−O(2′)	107.6(1)
O(3)−Mn(1)−O(2′)	91.1(1)	O(2)−Mn(1)−O(2′)	151.9(1)
O(3′)−Mn(1)−O(1′)	94.7(1)	O(3)−Mn(1)−O(1′)	150.2(1)
O(2)−Mn(1)−O(1′)	99.5(1)	O(2′)−Mn(1)−O(1′)	59.2(1)
O(3′)−Mn(1)−O(1)	150.2(1)	O(3)−Mn(1)−O(1)	94.7(1)
O(2)−Mn(1)−O(1)	59.2(1)	O(1′)−Mn(1)−O(1)	88.4(1)
C(2)−C(1)−P(2)	112.6(4)	C(2)−C(1)−P(1)	117.2(4)
P(2)−C(1)−P(1)	130.0(3)	O(1)−C(2)−O(2)	121.0(4)
O(1)−C(2)−C(1)	121.3(5)	O(2)−C(2)−C(1)	117.6(4)
O(1)−C(2)−Mn(1)	62.4(2)	O(2)−C(2)−Mn(1)	58.6(2)
C(2)−O(1)−Mn(1)	88.2(3)	C(2)−O(2)−Mn(1)	91.6(3)
P(3)−O(3)−Mn(1)	149.2(2)		

4 Conclusion

The difficulties to characterize or even to obtain complexes of the general type $[(L)_xM{\leftarrow}\mathbf{1}]^n$ either with low valent transition metal carbonyl compounds or with other Lewis acids probably is the result of the high reactivity of such species. Calculations have shown that **1** has a strong proton affinity of 280.0 kcal/mol but for the suggested complexes $[(CO)_5W{\leftarrow}\mathbf{1}]$ or $[Cl_2Be{\leftarrow}\mathbf{1}]$ similarly high proton affinities of 254 kcal/mol were calculated, a consequence of the second HOMO orbital of **1** [25]. Although **1** is stable in THF solution we know from various experiments that its addition compounds are able to abstract protons from solvents like THF, halocarbons, DME, DMSO, and related ones to produce the cation $(\mathbf{1}H)^+$; even the stable complexes $[(CO)_nNi{\leftarrow}\mathbf{1}]$ (n = 2, 3) deprotonate CH_2Cl_2 with cation forma-

Fortsetzung Table 3 Selected bond lengths/pm and angles/° in the cation of $\mathbf{3}\cdot 4C_6H_6$

Mn(1)−O(5)	208.8(2)	Mn(1)−O(6)	210.5(2)
Mn(1)−O(1)	219.7(2)	Mn(1)−O(3)	220.0(2)
Mn(1)−O(4)	226.1(2)	Mn(1)−O(2)	227.1(2)
Mn(1)−C(40)	256.2(4)	Mn(1)−C(2)	256.2(3)
C(2)−O(1)	127.4(4)	C(2)−O(2)	126.9(4)
C(1)−C(2)	147.8(4)	C(1)−P(2)	172.4(4)
C(1)−P(1)	172.8(4)	C(40)−O(3)	128.5(4)
C(40)−O(4)	126.4(4)	C(39)−C(40)	147.8(5)
C(39)−P(3)	172.4(3)	C(39)−P(4)	179.5(3)
O(5)−P(5)	149.5(3)	O(6)−P(6)	149.4(2)
O(5)−Mn(1)−O(6)	93.5(1)	O(5)−Mn(1)−O(1)	92.36(9)
O(6)−Mn(1)−O(1)	110.97(9)	O(5)−Mn(1)−O(3)	108.64(9)
O(6)−Mn(1)−O(3)	92.66(9)	O(1)−Mn(1)−O(3)	147.53(9)
O(5)−Mn(1)−O(4)	93.25(9)	O(6)−Mn(1)−O(4)	152.21(9)
O(1)−Mn(1)−O(4)	95.66(8)	O(3)−Mn(1)−O(4)	59.67(8)
O(5)−Mn(1)−O(2)	151.84(9)	O(6)−Mn(1)−O(2)	96.07(9)
O(1)−Mn(1)−O(2)	59.49(8)	O(3)−Mn(1)−O(2)	97.33(9)
O(4)−Mn(1)−O(2)	90.56(9)	C(2)−O(1)−Mn(1)	91.2(2)
C(2)−O(1)−Mn(1)	88.0(2)	C(2)−C(1)−P(2)	116.3(3)
C(2)−C(1)−P(1)	113.0(3)	P(2)−C(1)−P(1)	130.6(2)
O(2)−C(2)−O(1)	121.3(3)	O(2)−C(2)−C(1)	121.1(3)
O(1)−C(2)−C(1)	117.5(3)	C(40)−O(3)−Mn(1)	90.7(2)
C(40)−O(4)−Mn(1)	88.5(2)	C(40)−C(39)−P(3)	112.8(3)
P(3)−C(39)−P(4)	131.2(2)	O(4)−C(40)−O(3)	121.1(3)
O(4)−C(40)−C(39)	121.3(3)	O(3)−C(40)−C(39)	117.6(3)
P(5)−O(5)−Mn(1)	150.6(2)	P(6)−O(6)−Mn(1)	150.2(2)

tion [26]. In the reaction of **1** with $[Mn_2(CO)_{10}]$ proton abstraction proceeds more rapidly from THF than from DME, and the alternative but slow competitive Wittig reaction becomes important. This is also the case in benzene or toluene solution but the reaction remains incomplete. If we assume the formation of **[Mn]←1** intermediates in the first step such as the CO substitution product $[(CO)_5Mn(CO)_4Mn\leftarrow\mathbf{1}]$ proton abstraction from solvents becomes plausible but the related protonated complexes **[Mn]←1**H^+ are unstable in this case and decompose with release of the weak nucleophile $(\mathbf{1}H)^+$ finally with formation of **2**. Recently, we could show that the cation $(HC\{PPh_3\}_2)^+$ is able to serve as a ligand to Ag^+ if coordinating anions are absent. Thus, with $Ag[BF_4]$ and $(HC\{PPh_3\}_2)[BF_4]$ the new trication $[Ag(\mathbf{1}H)_2]^{3+}$ was produced [10]. These properties and the insolubility of adducts of **1** in non polar hydrocarbons limits the scope of synthesis and characterization.

However, if the reaction pathway is that of a Wittig reaction as with some carbonyl compounds, the formation of $OPPh_3$ opens the way to the adduct $O_2C\leftarrow\mathbf{1}$ according to equations 2 and 3 and subsequent formation of complexes with this ligand. The isolation of the unusual complex **3** from both the polar DME solution and the non polar benzene solution is a hint that this neutral 2:2 ligand combination of $O_2CC(PPh_3)_2$ and $OPPh_3$ in **3** is lowest in energy among others with different ones such as possible 3:0, 1:4, or 0:6 ligand arrangements.

An alternative route, the heterolytic splitting of the Mn-Mn bond by **1** to produce $[(CO)_5Mn(C\{PPh_3\}_2)][Mn(CO)_5]$ like the disproportion of $[Co_2(CO)_8]$ induced by an *N*-heterocyclic carbene (NHC) was not observed [27].

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. **1** was prepared according to the modified literature procedure [28]; commercially available $[Mn_2(CO)_{10}]$ was sublimed prior to use.

Reaction of $[Mn_2(CO)_{10}]$ with 1 in THF: 0.66 g (1.22 mmol) of **1** and 0.34 g (1.10 mmol) $[Mn_2(CO)_{10}]$ were stirred in about 6 ml THF for 0.5 h. All material has dissolved and a red solution was obtained. The ^{31}P NMR spectrum of this solution showed only a singlet at 20.6 ppm, indicating quantitative formation of the cation $(HC\{PPh_3\}_2)^+$. Layering of the solution with *n*-pentane produced a yellow red oil which crystallized to give orange yellow crystals of $\mathbf{2}\cdot$THF.

IR (Nujol mull, cm^{-1}): 1915 vs, 1896 vs, 1859 vs, 1840 vs, 1480 m, 1439 s, 1341 w, 1312 w, 1236 m, 1184 m, 1161 m, 1101 s, 1074 m, 1057 m, 1032 m, 1017 m, 993 m, 909 m, 804 m, 760 w, 743 m, 720 m, 683 s, 656 s, 559 w, 538 w, 517 w, 494 m.

Reaction of $[Mn_2(CO)_{10}]$ with 1 in DME: 0.32 g (0.60 mmol) of **1** and 0.24 g (0.60 mmol) $[Mn_2(CO)_{10}]$ were stirred in about 4 ml DME, which was distilled over potassium prior to use. The resulting suspension (**1** is only slightly soluble in DME) was stirred mechanically at room temperature. After four days all material has dissolved and an orange solution was obtained. The ^{31}P NMR spectrum of the solution showed signals (relative intensities in brackets) at 61.2 (0.23), 46.3 (1.00), 26.0 (2.56), 21.6 (6.20), 20.1 (1.39), 18.8 (1.07), −3.65 (1.18), and −10.5 (1.30) ppm. The solution was layered with *n*-pentane. After several days yellow needles separated along with an orange oil. The crystals turned out to be the salt-like complex $\mathbf{3}\cdot$1.75DME. The oil was separated and dissolved in DME and filtered. In the ^{31}P NMR spectrum of the solution only a singlet at 21.6 ppm was found. Layering with *n*-pentane produced large yellow blocks of **2**.

IR (Nujol mull, cm^{-1}) of **2**: 1915 sh, 1896 vs, 1859 vs, 1840 vs, 1481 m, 1437 s, 1312 w, 1231 m, 1185 m, 1104 s, 1029 m, 1012 m, 993 s, 744 s, 717 s, 683 vs, 658 vs, 559 s, 533 s, 515 s, 497 s.

Reaction of $[Mn_2(CO)_{10}]$ with 1 in benzene: 0.27 g (0.60 mmol) $[Mn_2(CO)_{10}]$ was added to a solution of 0.30 g (0.60 mmol) of **1** in about 7 ml of dry benzene. Immediately the color of the solution turned from yellow to orange red. The mixture was stirred magnetically; after about 30 min crystals of unreacted **1**, small amounts of a yellow precipitate, and a red brown oil were detected in the mixture. The mixture was stirred for about ten days at room temperature. The ^{31}P NMR spectrum of the benzene solution showed singlets (relative intensities in brackets) at 26.3(1), 20.6(1.2), −3.8(2.6), and −13.0(0.4) ppm; the main signal belongs to unreacted **1**. The signals at 26.3 and −13.0 ppm can be assigned to $OPPh_3$ and a Wittig product of the type **[Mn]**$=C=C=PPh_3$. The mixture was filtered from the precipitate. The filtrate, consisting of the oil and the benzene solution, was layered with *n*-pentane. After about two weeks, yellow orange crystals of $\mathbf{3}\cdot 4C_6H_6$ have grown from the oil.

IR (Nujol mull, cm^{-1}): 2045 m, 1975 m, 1887 vs, 1851 vs, 1588 m, 1576 m, 1531 m, 1501 m, 1481 s, 1437 s, 1354 m, 1312 w, 1233 w, 1186 m, 1163 w, 1103 s, 1030 w, 995 m, 745 s, 719 s, 683 s, 658 s, 559 w, 544 m, 525 m, 515 m, 502 m.

The nature of the precipitate is still unknown. It is soluble in CH_2Cl_2, but in the ^{31}P NMR spectrum only the signal of the cation $(HC\{PPh_3\}_2)^+$ was found as a result of the reaction with the solvent.

Reaction of $[Mn_2(CO)_{10}]$ with 1 in toluene: 0.87 g (1.63 mmol) of **1** and 0.62 g (1.59 mmol) $[Mn_2(CO)_{10}]$ were separately dissolved in about 5 ml toluene and the solutions were combined; a color change from yellow to red was observed. The mixture was stirred for 24 h. The ^{31}P NMR spectrum of the solution showed the signal of unchanged **1** as the main product; additionally, the signals of $OPPh_3$ and a Wittig product have appeared in about 1 % of the main signal.

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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 682167 (**2**), CCDC 682168 (**2**·THF), CCDC 682169 (**3**·1.75DME), and CCDC 682170 (**3**·$4C_6H_6$). (Fax: (+44)1223-336-033; E-mail: **deposit@ccdc.cam.ac.uk**).

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