On the Reaction of $C(PPh_3)_2$ with $[Co_2(CO)_8]$: Formation and Structure of an Unusual Tetranuclear Cluster

Wolfgang Petz, Kirstin Wenck, and Bernhard Neumüller

Fachbereich Chemie der Philipps-Universität Marburg, Hans Meerwein-Straße, 35032 Marburg, Germany

Reprint requests to Prof. W. Petz. E-mail: petz@staff.uni-marburg.de or
Prof. B. Neumüller. E-mail: neumuell@chemie.uni-marburg.de

Z. Naturforsch. **2007**, *62b,* 413 – 418; received December 3, 2006

Dedicated to Prof. Helgard G. Raubenheimer on the occasion of his 65th birthday

The reaction of the carbodiphosphorane $C(PPh_3)_2$ (**1**) with $[Co_2(CO)_8]$ results in the formation of the salt-like complex $(HC\{PPh_3\}_2)[Co(CO)_4]$ (**2**) in high yield if THF is used as the solvent. The proton of the cation stems from THF degradation. When the reaction is carried out in toluene, the tetranuclear cluster $[Co_4(CO)_{10}(PPh_3)(\mu_4\text{-}CCPPh_3)]$ (**3**) is formed in low yield as the only complex which could be identified by X-ray analysis. The solvate $\mathbf{3}\cdot C_7H_8$ crystallizes in the triclinic space group $P\bar{1}$ with a = 1040.8(2), b = 1387.4(2), c = 1923.0(2) pm, α = 71.96(1)°, β = 88.69(1)°, γ = 71.46(1)°, Z = 2. The structure of the cluster with 64 CVE is that of a "spiked triangle" in which the triphenylphosphonioacetylide $CCPPh_3$ acts as a six-electron donor and the bonding mode is that of a μ_4-η^2 coordination.

Key words: Tetranuclear Cobalt Cluster, Carbodiphosphorane, Phosphacumulene Ligand, Proton Abstraction, Crystal Structure

Introduction

The double ylide $C(PPh_3)_2$ (**1**) has been known since 1961 [1], and for its solid state a bent structure with an approximately sp^2-hybridized carbon atom was established by X-ray diffraction [2]. Thus, in accord with a lone pair of electrons, the chemistry of **1** is mainly governed by the properties of a typical Lewis base, and various electron acceptor components produce adducts of the type $E{\leftarrow}C(PPh_3)_2$, in which E can represent an element (S, Se [3]), a cation (I^+ [4], Cl^+, H^+ [5]), a heteroallene [6], a group 13 compound ($InMe_3$, $AlBr_3$ [5]), or various transition metal fragments ($[ReO_3]^+$ [7], Cp^*Cu [8], XAu [9], $(CO)_nNi$ [10]). Several reviews concerning the chemistry of ylides including **1** have been published [11]. In the case of metal carbonyl compounds the reaction of **1** not only leads to CO substitution and formation of ylide complexes as in $[(CO)_nNi(C\{PPh_3\}_2)]$ (n = 2, 3) [10], but to a nucleophilic attack of **1** at a carbonyl carbon atom to produce the metal bonded triphenylphosphonioacetylide ligand $CCPPh_3$ in a "Wittig-type" manner under elimination of $OPPh_3$, similar to the action of a hard base as reported for $[Fe(CO)_5]$ [12] and $[BrMn(CO)_5]$ [13]. With the two options of reaction pathways for **1**, we now turned to the transition metal carbonyl $[Co_2(CO)_8]$, which is located between the carbonyls of Fe and Ni. The results of reactions in various solvents are reported here.

Results and Discussion

The results of the reaction of **1** with $[Co_2(CO)_8]$ strongly depend on the solvent and do not lead to a CO substitution as in the case of $[Ni(CO)_4]$. If THF is used, H^+ abstraction from the solvent is observed with formation of the salt $(HC\{PPh_3\}_2)[Co(CO)_4]$ (**2**). The ^{31}PNMR spectrum of the solution exhibits only one singlet at 20.3 ppm for the cation. The formation of the cation is quantitative and can not be explained with partial hydrolysis of an initial reaction product. The mechanism is not clear, but it seems likely that in the first step the complex $[Co(CO)_4(C\{PPh_3\}_2)][Co(CO)_4]$ is formed, which apparently is highly reactive (eq. 1 and eq. 2).

$$[Co_2(CO)_8] + C(PPh_3)_2 \rightarrow [Co(CO)_4(C\{PPh_3\}_2)][Co(CO)_4] \quad (1)$$

0932–0776 / 07 / 0300–0413 $ 06.00 © 2007 Verlag der Zeitschrift für Naturforschung, Tübingen · http://znaturforsch.com

$$[Co(CO)_4(C\{PPh_3\}_2)][Co(CO)_4] + H^+ \rightarrow (HC\{PPh_3\}_2)[Co(CO)_4] + \ldots \quad (2)$$

2

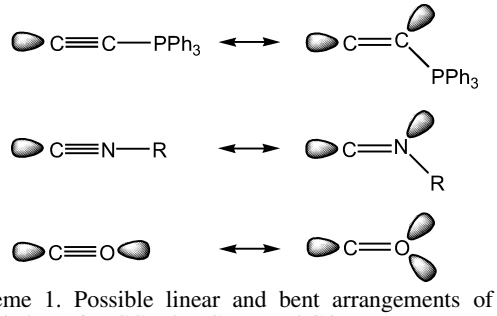
As yet, we were unable to confirm the existence of this intermediate. $[Co_2(CO)_8]$is known to react with various Lewis bases L with disproportion into salts $[Co(CO)_4L][Co(CO)_4]$ in the first step [14]. For the formation of the cation $(HC\{PPh_3\}_2)^+$ different pathways can be discussed. The cation first produced may undergo a homolytic splitting with formation of the radicals $[Co(CO)_4]^\bullet$ and $(C\{PPh_3\}_2)^{+\bullet}$; the latter may than deprotonate a solvent molecule. An alternative is taking up a proton from the solvent at the coordinating carbon atom and formation of the dication $[Co(CO)_4(HC\{PPh_3\}_2)]^{2+}$. Very recently we have shown that the cation $(HC\{PPh_3\}_2)^+$ itself can serve as a ligand for transition metals in the absence of further coordinating anions. Thus, with $AgBF_4$ the trication $[Ag(HC\{PPh_3\}_2)_2]^{3+}$was obtained upon reaction with $(HC\{PPh_3\}_2)[BF_4]$ [15]. After deprotonation of THF, the remaining anionic species may lose OH^- to produce 1,3-butadiene. The overall release of H_2O from THF under catalytic conditions and formation of 1,3-butadiene or other species was described earlier [16]. Similar unusual solvent degradation reactions were also observed when group 6 carbonyl compounds were treated with **1** in THF solution; final support for this mechanism is the detection of carbonato complexes in reactions of **1** with $[Mo(CO)_6]$, which can only be rationalized by the presence of OH^- ions in the reaction mixture [17]. Thus, the colorless compound **2** is finally formed through the action of water.

However, as yet we were not able to detect the butadiene in the reaction mixture, and another mode of degradation of THF with release of H^+ may also be considered. Theoretical considerations have shown that **1** has a high proton affinity [18], and during our studies concerning the chemistry of **1** and the related CS_2, CO_2 and COS adducts we have often observed the formation of the cation $(HC\{PPh_3\}_2)^+$ if THF or halogenated hydrocarbons such as dichloromethane were used as solvents [6].

To avoid any H abstraction from a source like THF we carried out the reaction of **1** with $[Co_2(CO)_8]$ in toluene. The ^{31}P NMR spectrum of the initial reaction mixture showed two signals at 23.7 and 16.0 ppm in an approximately 2 : 1 ratio. The low field signal could be assigned to $OPPh_3$, which indicates that in the first step a nucleophilic attack of **1** at a carbonyl carbon atom has occurred followed by a Wittig-type reaction with elimination of $OPPh_3$ and formation of the $CCPPh_3$ ligand similar to the results of the reactions of **1** with $[Fe(CO)_5]$ [12] or $[Mn(CO)_5Br]$ [13]. From the solution, on layering with *n*-pentane and standing for some weeks, small amounts of reddish brown crystals separated, which were identified as the tetranuclear cluster $[Co_4(CO)_{10}(PPh_3)(\mu_4\text{-}CCPPh_3)]$ (**3**). Unfortunately, the crystals of **3** could not be redissolved in toluene. The initial signal in the ^{31}P NMR spectrum probably does not belong to the new tetranuclear cluster complex which is expected to show two signals. For compounds with a $(CO)CoPPh_3$ fragment a low field signal in the ^{31}P NMR spectrum at about 70 ppm is expected [19], and the $CCPPh_3$ group normally resonates at about −10 ppm.

The IR spectrum of **3** exhibits several strong bands between 1948 and 2045 cm^{-1}, which can be assigned to vibrations of terminal CO groups. Three medium strong bands at 1800, 1819, and 1839 cm^{-1} can be attributed to the three bridging CO ligands. A medium strong band at 1414 cm^{-1} may be due to the vibration of the CC multiple bond of the acetylide ligand [20]. The PPh_3 ligand found in **3** may originate from a reduction of $OPPh_3$ with $[Co_2(CO)_8]$ or other low valent cobalt carbonyl fragments; free **1** as a PPh_3 source has not yet been observed.

The difference in the reaction of **1** with $[Ni(CO)_4]$ and $[Fe(CO)_5]$ can be rationalized by the more electrophilic nature of the carbonyl carbon atoms in the iron species because fewer *d* electrons are present for back bonding into a larger number of CO groups. For the dimeric cobalt carbonyl complex, the experiment establishes a close similarity to the iron carbonyl which has in common the formation of the phosphacumulene or acetylide ligand $CCPPh_3$. This interesting ligand is composed of a C_2 unit, which attains 10 electrons by means of the pair of electrons from PPh_3 and thus can



Scheme 1. Possible linear and bent arrangements of the isolobal species $CCPPh_3$, CNR, and CO.

Table 1. Crystal and refinement data for **2** and $\mathbf{3}\cdot C_7H_8$.

	2	$\mathbf{3}\cdot C_7H_8$
Formula	$C_{41}H_{31}CoO_4P_2$	$C_{55}H_{38}Co_4O_{10}P_2$
M_r	708.57	1156.56
Crystal size [mm^3]	0.31×0.30×0.10	0.19×0.13×0.06
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$ (Nr. 2)	$P\bar{1}$ (Nr. 2)
a [pm]	985.2(1)	1040.8(2)
b [pm]	1152.0(1)	1387.4(2)
c [pm]	1617.6(2)	1923.0(2)
α [deg]	72.73(1)	71.96(1)
β [deg]	80.58(1)	88.69(1)
γ [deg]	86.20(1)	71.46(1)
V [$pm^3\cdot10^6$]	1729.2(3)	2494.5(5)
Z	2	2
D_{calc} [g cm^{-3}]	1.361	1.54
Diffractometer	IPDS II (Stoe)	IPDS II (Stoe)
Temperature [K]	193	193
$\mu(MoK_\alpha)$ [cm^{-1}]	6.3	14.3
Absorption correction	numerical	numerical
$2\theta_{max}$ [deg]	52.12	52.46
hkl range	$-11 \le h \le 11$	$-12 \le h \le 12$
	$-14 \le k \le 14$	$-16 \le k \le 16$
	$-19 \le l \le 19$	$-23 \le l \le 22$
Measured reflexions	17166	24591
Unique reflexions	6302	9960
R_{int}	0.046	0.0666
Reflexions with $F_0 \ge 4\sigma(F_0)$	3883	5401
Refined parameters	438	670
Structure solution	– Patterson Method –	
	– SHELXTL-Plus [32] –	
Refinement on F^2	– SHELXL-97 [33] –	
H atoms	[a]	[b]
R_1	0.0333	0.0397
wR_2 (all data)	0.0663	0.0641
$\Delta\rho_{fin}$ [e $pm^{-3}\times10^{-6}$]	0.25	0.43

[a] Refined in calculated positions with a common displacement parameter; free refinement of H1; [b] refined in calculated positions with a common displacement parameter.

be considered to be isoelectronical with isocyanides or CO as depicted in Scheme 1.

Efforts were also made recently to isolate free $CCPPh_3$, which was found to be stable only in solution at very low temperature [21]. However, till now the coordination chemistry of $CCPPh_3$ has been poorly developed and only few complexes are known. No complex formation was described starting from the free ligand. Like CO, this ligand can coordinate in a terminal manner with donation of two electrons [12, 13] or, as in the trinuclear complex $[Fe_3(CO)_9(CCPPh_3)]$, it can bridge the three metal atoms in a μ_3-η^2 manner and act as a six-electron donor as required for a satisfactory electron count [12]. To our knowledge, a similar CO coordination is only realized in the trinuclear complex $[Cp_3Nb_3(CO)_3(\mu_3\text{-CO})]$, where the bridging CO group also donates six electrons [22].

Table 2. Selected bond lengths (pm) and angles (deg) for the salt **2** with estimated standard deviations in parentheses.

Cation:			
P(1)-C(5)	169.3(3)	P(1)-C(6)	179.2(2)
P(1)-C(12)	180.2(2)	P(1)-C(18)	179.8(2)
P(2)-C(5)	168.8(3)	P(2)-C(24)	179.8(2)
P(2)-C(30)	180.6(2)	P(2)-C(36)	179.4(2)
C(5)-H(1)	82(3)		
Anion:			
Co(1)-C(1)	173.6(3)	Co(1)-C(2)	175.7(3)
Co(1)-C(3)	174.2(3)	Co(1)-C(4)	173.9(3)
O(1)-C(1)	116.0(3)	O(2)-C(2)	115.4(3)
O(3)-C(3)	115.9(3)	O(4)-C(4)	116.3(3)
Cation:			
C(5)-P(1)-C(6)	111.8(1)	C(5)-P(1)-C(12)	112.4(1)
C(5)-P(1)-C(18)	112.0(1)	C(6)-P(1)-C(12)	106.6(1)
C(6)-P(1)-C(18)	107.6(1)	C(12)-P(1)-C(18)	106.0(1)
C(5)-P(2)-C(24)	109.6(1)	C(5)-P(2)-C(30)	114.9(1)
C(5)-P(2)-C(36)	113.3(1)	C(24)-P(2)-C(30)	106.3(1)
C(24)-P(2)-C(36)	104.5(1)	C(30)-P(2)-C(36)	107.6(1)
P(1)-C(5)-P(2)	129.3(2)	P(1)-C(5)-H(1)	116(2)
P(2)-C(5)-H(1)	115(2)		
Anion:			
C(1)-Co(1)-C(2)	109.2(1)	C(1)-Co(1)-C(3)	113.1(1)
C(1)-Co(1)-C(4)	108.7(1)	C(2)-Co(1)-C(3)	106.8(1)
C(2)-Co(1)-C(4)	112.0(1)	C(3)-Co(1)-C(4)	107.1(1)

Crystal structures

In order to get a deeper insight into the features of the compounds, the structures of **2** and $\mathbf{3}\cdot C_7H_8$ were determined by single crystal X-ray diffraction measurements. Colorless crystals of **2** were obtained at r. t. by layering the filtered THF solution with *n*-pentane, and brownish black crystals of $\mathbf{3}\cdot C_7H_8$ deposited on standing of a toluene solution of the reaction mixture for several days. The toluene molecule in $\mathbf{3}\cdot C_7H_8$ is disordered but could be refined in two split positions (0.6 : 0.4). The ORTEP views of **3** are depicted in Fig. 1. Although the salt-like solvent-free compound **2** has not been described earlier, the structure is not shown because cation and anion of **2** are well known and related compounds with different counterions have already been published [23, 24]. Details of the structure determinations are collected in Table 1; bond lengths and angles are summarized in the Tables 2 and 3.

Molecular structure of ***2***

The ionic compound **2** forms colorless crystals. There are no remarkable interionic contacts; the shortest C–H···O distance occurs between a phenyl proton and an oxygen atom with a C···O separation of

Table 3. Selected bond lengths (pm) and angles (deg) for $\mathbf{3} \cdot C_7H_8$ with estimated standard deviations in parentheses.

Co(1)-Co(2)	249.6(1)	Co(1)-Co(3)	252.3(1)
Co(2)-Co(3)	249.8(1)	Co(3)-Co(4)	252.9(1)
Co(1)-C(1)	202.0(4)	Co(1)-C(2)	208.9(4)
Co(1)-C(9)	184.4(4)	Co(2)-C(1)	200.9(4)
Co(2)-C(2)	205.3(4)	Co(2)-C(7)	197.7(4)
Co(3)-C(2)	197.7(4)	Co(3)-C(7)	187.7(4)
Co(3)-C(10)	201.6(4)	Co(3)-C(9)	205.3(4)
Co(4)-C(2)	202.7(4)	Co(4)-P(2)	222.4(1)
P(1)-C(1)	173.9(4)	Co(4)-C(10)	187.6(4)
O(10)-C(10)	117.2(5)	O(7)-C(7)	118.4(4)
C(1)-C(2)	136.4(4)	O(9)-C(9)	117.9(4)
C(1)-Co(1)-Co(2)	51.5(1)	C(2)-Co(1)-Co(2)	52.3(1)
C(1)-Co(1)-Co(3)	85.3(1)	C(2)-Co(1)-Co(3)	49.7(1)
C(1)-Co(2)-Co(1)	51.9(1)	C(2)-Co(2)-Co(1)	53.6(1)
C(1)-Co(2)-Co(3)	86.2(1)	C(2)-Co(2)-Co(3)	50.3(1)
C(2)-Co(3)-Co(2)	53.1(1)	C(2)-Co(3)-Co(1)	53.7(1)
C(2)-Co(3)-Co(4)	51.7(1)	C(2)-Co(4)-Co(3)	50.0(1)
Co(1)-Co(2)-Co(3)	60.7(1)	Co(2)-Co(3)-Co(1)	59.6(1)
Co(2)-Co(3)-Co(4)	95.3(1)	Co(1)-Co(3)-Co(4)	99.0(1)
P(2)-Co(4)-Co(3)	122.5(1)	P(2)-Co(4)-C(2)	172.3(1)
P(2)-Co(4)-C(10)	85.4(1)	P(2)-Co(4)-C(12)	95.2(1)
P(2)-Co(4)-C(11)	90.1(1)	C(1)-Co(1)-C(2)	38.7(2)
C(1)-Co(2)-C(2)	39.2(2)	C(2)-Co(4)-C(10)	89.3(2)
C(2)-Co(4)-C(11)	88.9(2)	C(2)-Co(4)-C(12)	91.9(2)
Co(1)-C(1)-P(1)	129.2(2)	P(1)-C(1)-C(2)	137.0(3)
Co(2)-C(1)-P(1)	141.2(2)	Co(1)-C(1)-C(2)	73.4(2)
Co(1)-C(1)-Co(2)	76.6(1)	Co(2)-C(1)-C(2)	72.2(2)
Co(1)-C(2)-Co(3)	76.7(1)	Co(3)-C(2)-C(1)	135.5(3)
Co(1)-C(2)-Co(2)	74.1(1)	Co(1)-C(2)-C(1)	67.9(2)
Co(1)-C(2)-Co(4)	137.9(2)	Co(2)-C(2)-Co(4)	131.1(2)
Co(2)-C(2)-Co(3)	76.6(1)	Co(3)-C(2)-Co(4)	78.3(2)
Co(2)-C(2)-C(1)	68.6(2)	Co(4)-C(2)-C(1)	146.0(3)

353 pm. The cobalt atom in the anion $[Co(CO)_4]^-$ is in a distorted tetrahedral environment; the six C–Co–C angles vary between 106.8 and 113.0°, the mean Co–C and C–O distances are 175.8 and 115.6 pm, respectively. In the cation $(HC\{PPh_3\}_2)^+$ the P(1)–C(5)–P(2) angle amounts to 128.9° similar to that found in related salts with this cation [23]. The difference between the P–C distances to C(5) and to the phenyl carbon atoms amounts to about 10 pm, and the shorter bond lengths to the ylidic carbon atom indicate some double bond character; however, relative to the neutral carbodiphosphorane $C(PPh_3)_2$, the presence of the proton at the ylidic carbon atom C(5) leads to an increase of these bond lengths by about 8 pm [2].

Molecular structure of ***3***

The cluster core is that of a spiked triangle (Fig. 1). No close intermolecular contacts exist between the molecules. The cluster core is electronically precise with a total number of 64 CVE's, the magic electron

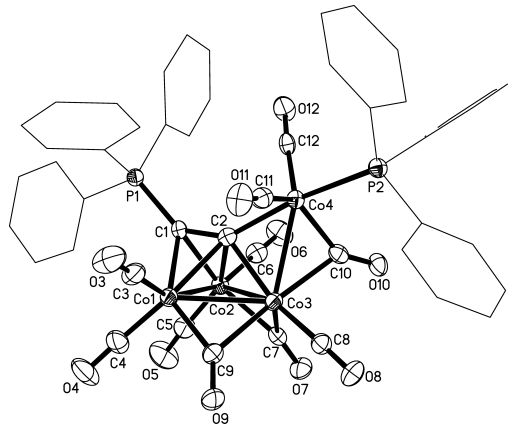


Fig. 1. Molecular structure of $\mathbf{3} \cdot C_7H_8$ showing the atom numbering scheme. The ellipsoids are drawn at the 40 % probability level. The H atoms at the phenyl groups are omitted for clarity, and the solvent molecule is not shown.

number being attained with the $CCPPh_3$ ligand acting as a six-electron donor. All bridging CO groups are placed asymmetrically and the differences between the Co–C bond lengths in a bridge are 10 pm [C(7)], 14 pm [C(10)], and 21 pm [C(9)]. The triangular system can be compared with the basal Co_3 core of $[Co_4(CO)_{12}]$ [25] or of $[Co_3(CO)_9(\mu_3\text{-CR})]$ compounds [26] containing a μ-carbyne ligand; the ligand arrangement along the Co(3)–Co(4) bond resembles that of $[Co_2(CO)_8]$ [27].

The Co–Co bond lengths in the basal Co_3 plane of **3** are slightly longer than in related compounds. Two CO groups bridge edges of the basal Co_3 triangle, whereas the third one is bridging the spiked Co–Co bond. Molecule **3** does not contain a plane of symmetry indicating chirality, and the unit cell is composed of a pair of enantiomers. For the $CCPPh_3$ ligand the unusual and not yet described μ_4-η^2 coordination is achieved, and its terminal C(2) atom is connected to C(1) and all four cobalt atoms; to the latter with nearly equal distances. The carbon atoms C(1) and C(2) form a total of six bonds to Co atoms, and the Co–C bond lengths vary between 198 and 209 pm. With its lone pair of electrons, the carbon atom C(2) bridges two Co atoms symmetrically, whereas in the related iron complex $[Fe_3(CO)_9(C_2PPh_3)]$ this carbon atom is only connected to one further Fe atom resulting in a μ_3-η^2 coordination mode for the $CCPPh_3$ ligand. The C(1)–C(2) bond length amounts to 136.4(4) pm corresponding to an elongated olefinic double bond, and is longer than in the related trinuclear iron complex [132.5(8)] [12]; the same is true for the adja-

cent P–C(1) bond, which is slightly longer in the cobalt complex. Thus, the μ_4 coordination mode of the $CCPPh_3$ ligand leads to an increased electron release with respect to the μ_3 mode. A similar μ_4-η^2 coordination was also found by us recently with the CO ligand, but the arrangement of the metal atoms (2 lithium atoms at the oxygen atom and an Fe_2 unit at the carbon atom) differs markedly from that in **3** [28]. Thus, the μ_4-η^2 coordination of the $CCPPh_3$ ligand found in **3** is unique. The C–C–P angle amounts to 137.0(3)° and is similar to that in $[Fe_3(CO)_9(CCPPh_3)]$ [138.7(5)] but more acute than in $[(CO)_4Fe(CCPPh_3)]$ [162.1(3)] and $[Br(CO)_4Mn(CCPPh_3)]$ [164.0(12)], were $CCPPh_3$ acts as a terminal ligand. Similar as in solid $[Co_2(CO)_8]$, the spiked Co–Co bond has two bridges, one CO and one $CCPPh_3$ group, and the dihedral angle between the planes C(2)Co(3)Co(4) and C(10)Co(3)Co(4) amounts to 130°, which is close to the dihedral angle in $[Co_2(CO)_8]$ (127°). The PPh_3 group at Co(4) is probably formed in the reduction of $OPPh_3$ with cobalt carbonyl species. The Co–P distance corresponds to that in *trans*-$[(Ph_3P)_2Co_2(CO)_6]$ [29].

Conclusion

With the exception of the carbonyl complexes $[(CO)_2Ni(C\{PPh_3\}_2)]$ and $[(CO)_3Ni(C\{PPh_3\}_2)]$ no carbonyl complexes of the type $[(CO)_xM(C\{PPh_3\}_2)]^n$ (M = group 6 to group 9 transition metals) containing $C(PPh_3)_2$, **1**, as a ligand could as yet be synthesized and their structure confirmed by X-ray diffraction. This is probably due to the poor π acceptor properties of **1** according to the occupied *p* orbital at the ylidic carbon atom. Complexes of this type are probably formed as reaction intermediates but appear to be strong bases with the option to abstract protons from a variety of solvents such as THF or CH_2Cl_2. The resulting proton acceptor complex $[(CO)_xM(HC\{PPh_3\}_2)]^{n+1}$ is less stable than the related silver complex [15] and decomposition occurs with elimination of $(HC\{PPh_3\}_2)^+$. Even the complexes $[(CO)_2Ni(C\{PPh_3\}_2)]$ and $[(CO)_3Ni(C\{PPh_3\}_2)]$ are not stable in CH_2Cl_2 but immediately produce the cation $(HC\{PPh_3\}_2)^+$. All attempts to isolate the related complex $[(CO)_4Fe(C\{PPh_3\}_2)]$ have failed [30]. Further endeavors to find the appropriate conditions for the preparation of $[(CO)_xM(C\{PPh_3\}_2)]^n$ complexes (or related species $[(CO)_xM(HC\{PPh_3\}_2)]^{n+1}$) for group 6 to 9 transition metals and to prove their structure by X-ray diffraction are currently in progress.

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 NMR spectra we used the instruments Bruker AMX 500 and AC 200. Elemental analyses were performed by the analytical service of the Fachbereich Chemie der Universität Marburg (Germany). **1** was prepared according to a modified literature procedure [31] from $(ClC\{PPh_3\}_2)Cl$ and $P(NMe_2)_3$. Commercially available $[Co_2(CO)_8]$ was used without further purification.

*Formation of $(HC\{PPh_3\}_2)[Co(CO)_4]$ (**2**)*

A solution of **1** (0.83 g, 1.60 mmol) in 100 mL of THF was cooled to −78 °C. To this solution $[Co_2(CO)_8]$ (0.66 g, 1.90 mmol) was added and the mixture was stirred for 2 h. The dark red solution was allowed to warm to r. t.. After additional 2 h the mixture was filtered over diatomaceous earth. In the ^{31}P NMR spectrum of the solution only a singlet at 21.0 ppm was observed. The solution was layered with *n*-pentane, and after several weeks colorless crystals of **2** were obtained. Yield: 0.88 g (77 %). – IR (Nujol mull, cm^{-1}): ν = 1888 vs br, 1483 m, 1439 s, 1337 w, 1312 w, 1225 m, 1186 m, 1103 s, 1009 w, 989 m, 804 w, 793 w, 760 w, 743 s, 716 s, 692 ws, 554 ws, 523 s, 503 m, 490 m.

*Formation of $[Co_4(CO)_{10}(PPh_3)(\mu_4\text{-}CCPPh_3)]$ (**3**)*

To a suspension of **1** (1.00 g, 1.86 mmol) in 20 mL of toluene, which was precooled to −78 °C, was added 0.636 g (1.86 mmol) of $[Co_2(CO)_8]$. The mixture was stirred mechanically for about 1 h at this temperature and then allowed to warm to r. t. and stirred for additional 5 h. A brownish black reaction mixture was obtained, which was filtered from some insoluble material. The ^{31}P NMR spectrum of the solution showed two signals at 16.0 and 23.7 ppm in a 1 : 2 ratio. The solution was stored at −18 °C for about two weeks to afford reddish brown crystals of $\mathbf{3} \cdot C_7H_8$. Yield: *ca.* 0.04 g (3 %). The crystals could not be redissolved in toluene. – IR (Nujol mull, cm^{-1}): ν = 2045 s, 2000 vs br, 1987 vs, 1948 vs, 1887 m br, 1839 s, 1819 s, 1800 s, 1605 vw, 1586 vw, 1572 vw, 1495 w, 1480 m, 1436 s, 1414 m, 1378 m, 1097 s, 746 m, 727 vs, 692 vs, 546 m, 520 vs. – $C_{55}H_{38}Co_4O_{10}P_2$(1156.56): calcd. C 57.10, H 3.31; found C 55,78, H 3.06.

CCDC 628555 (**2**) and CCDC 628556 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

Financial support of this work was provided by the Deutsche Forschungsgemeinschaft. W. P. thanks the Max-

Planck-Society, Munich, Germany, for supporting this research project.

[1] F. Ramirez, N. B. Desai, B. Hansen, N. McKelvie, *J. Am. Chem. Soc*. **1961**, *83*, 3539 – 3540.

[2] a) A. T. Vincent, P. J. Wheatley, *J. Chem. Soc., Dalton Trans*. **1972**, 617 – 622; b) G. E. Hardy, J. I. Zink, W. C. Kaska, J. C. Baldwin, *J. Am. Chem. Soc*. **1978**, *100*, 8001 – 8002.

[3] H. Schmidbaur, C. E. Zybill, D. Neugebauer, *Angew. Chem*. **1982**, *94*, 321 – 322; *Angew. Chem. Int. Ed. Engl*. **1982**, *21*, 310 – 311.

[4] a) H. Schmidbaur, C. Zybill, D. Neugebauer, G. Müller, *Z. Naturforsch*. **1985**, *40b*, 1293 – 1300; b) W. Petz, K. Öxler, S. Heimann, B. Neumüller, *Z. Anorg. Allg. Chem*. **2007**, *633*, in press.

[5] W. Petz, C. Kutschera, S. Tschan, F. Weller, B. Neumüller, *Z. Anorg. Allg. Chem*. **2003**, *629*, 1235 – 1244.

[6] W. Petz, C. Kutschera, M. Heitbaum, B. Neumüller, G. Frenking, R. Tonner, *Inorg. Chem*. **2005**, *44*, 1263 – 1274.

[7] J. Sundermeyer, K. Weber, K. Peters, H. G. von Schnering, *Organometallics* **1994**, *13*, 2560 – 2562.

[8] C. Zybill, G. Müller, *Organometallics* **1987**, *6*, 2489 – 2494.

[9] a) H. Schmidbaur, C. E. Zybill, G. Müller, C. Krüger, *Angew. Chem*. **1983**, *95*, 753 – 755; *Angew. Chem. Int. Ed. Engl*. **1983**, *22*, 729 – 731; b) J. Vicente, A. R. Singhal, P. G. Jones, *Organometallics* **2002**, *21*, 5887 – 5900.

[10] W. Petz, F. Weller, J. Uddin, G. Frenking, *Organometallics* **1999**, *18*, 619 – 626.

[11] a) H. Schmidbaur, *Angew. Chem*. **1983**, *95*, 980 – 1000; *Angew. Chem. Int. Ed. Engl*. **1983**, *22*, 907 – 927; b) W. C. Kaska, *Coord. Chem. Rev*. **1983**, *48*, 1 – 58.

[12] W. Petz, F. Weller, *Z. Naturforsch*. **1996**, *51b*, 1598 – 1604.

[13] a) S. Z. Goldberg, E. N. Duessler, K. N. Raymond, *Inorg. Chem*. **1972**, *11*, 1397 – 1401; b) W. C. Kaska, D. K. Mitchell, R. F. Reichelderfer, W. D. Korte, *J. Am. Chem. Soc*. **1974**, *96*, 2847 – 2854.

[14] R. D. W. Kemmitt, D. R. Russel, *Comprehensive Organomet. Chem*. **1982**, *5*, 1 – 276.

[15] W. Petz, B. Neumüller, G. Frenking, R. Tonner, *Angew. Chem*. **2006**, *118*, 8206 – 8211; *Angew. Chem. Int. Ed. Engl*. **2006**, *45*, 8038 – 8042.

[16] W. Reppe, *Liebigs Ann. Chem. A*. **1955**, *596*, 1 – 224.

[17] W. Petz, B. Neumüller, F. Weller, unpublished results.

[18] G. Frenking, personal communication.

[19] S. E. Gibson, C. Johnstone, J. A. Loch, J. W. Steed, A. Stevenazzi, *Organometallics* **2003**, *22*, 5374 – 5377.

[20] J. Weidlein, U. Müller, K. Dehnicke, *Schwingungsfrequenzen I, Hauptgruppenelemente*, G. Thieme Verlag, Stuttgart, **1981**.

[21] H. J. Bestmann, W. Frank, C. Moll, A. Pohlschmidt, T. Clark, A. Göller, *Angew. Chem*. **1998**, *110*, 347 – 351; *Angew. Chem. Int. Ed. Engl*. **1998**, *37*, 338 – 342.

[22] W. A. Herrmann, H. Biersack, M. L. Ziegler, K. Weidenhammer, R. Siegel, D. Rehder, *J. Am. Chem. Soc*. **1981**, *103*, 1692 – 1699.

[23] Selected compounds with the cation $(HC\{PPh_3\}_2)^+$: a) W. Petz, F. Weller, *Z. Kristallogr*. **1997**, *212*, 157 – 158 for $([Fe_2(CO)_8]^{2-})$; b) Ref. [5] $([MeInCl_3]^-)$ and $([Me_3SnCl_2]^-)$; c) A. Schmidpeter, F. Zwaschka, W. S. Sheldrick, *Chem. Ber*. **1985**, *118*, 1078 – 1085 for $([P_2C_{10}N_{10}]^{2-})$.

[24] Selected compounds with the anion $[Co(CO)_4]^-$: a) W. Petz, F. Weller, *Z. Naturforsch*. **1991**, *46b*, 297 – 302 for $(C\{NMe_2\}_3)^+$; b) J. S. Merola, K. S. Kampo, R. A. Gentile, M. A. Modrick, *Inorg. Chim. Acta* **1989**, *165*, 87 – 90 for $[Cp_2Ti(THF)]^+$.

[25] a) C. H. Wei, L. F. Dahl, *J. Am. Chem. Soc*. **1966**, *88*, 1821 – 1822; b) C. H. Wei, *Inorg. Chem*. **1969**, *8*, 2384 – 2397.

[26] a) P. W. Sutton, L. F. Dahl, *J. Am. Chem. Soc*. **1967**, *89*, 261 – 268; b) F. Klanberg, W. B. Askew, L. J. Guggenberger, *Inorg. Chem*. **1968**, *7*, 2265 – 2271.

[27] a) G. G. Sumner, H. P. Klug, L. E. Alexander, *Acta Crystallogr*. **1964**, *17*, 732 – 742; b) P. C. Leung, P. Coppens, *Acta Crystallogr*. **1983**, *B39*, 535 – 542.

[28] B. Neumüller, W. Petz, *Organometallics* **2001**, *20*, 163 – 170.

[29] L. Brammer, J. C. Marque Rivas, C. D. Spilling, *J. Organomet. Chem*. **2000**, *609*, 36 – 43.

[30] W. Petz, unpublished results.

[31] R. Appel, F. Knoll, H. Schöler, H.-D. Wihler, *Angew. Chem*. **1976**, *88*, 769 – 770; *Angew. Chem. Int. Ed. Engl*. **1976**, *15*, 702 – 703.

[32] G. M. Sheldrick, SHELXTL-Plus (version 4.2), Siemens Analytical X-Ray Instruments Inc., Madison, Wisconsin (USA) **1990**.

[33] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**.