# The Structure of the Ligand Tri(1-cyclohepta-2,4,6-trienyl)phosphane, $P(C_7H_7)_3$, in the Hexafluoroacetylacetonato Copper(I) Complexes, $(hfac)Cu[P(C_7H_7)_3]_n$ ($n = 1, 2$)

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The reaction of $CuCl[P(C_7H_7)_3]$ (**1a**) with sodium hexafluoroacetylacetonate, Na(hfac), leads to $(hfac)Cu[P(C_7H_7)_3]$ (**2a**), which in the presence of excess $P(C_7H_7)_3$ (**a**) gives $(hfac)Cu[P(C_7H_7)_3]_2$ (**3a**). Whereas the 1:2 compound **3a** is a pseudo-tetrahedral copper(I) complex with relatively long Cu-P (224.85(10) and 223.75(10) pm) and Cu-O (212.7(3) and 212.0(3) pm) distances, the 1:1 complex **2a** may be described as having a distorted pseudo-trigonal coordination sphere (Cu-P 214.32(11) pm, Cu-O 196.6(3) and 208.1(3) pm), although one of the cyclohepta-2,4,6-trienyl substituents develops a weak additional interaction with the metal through its central C=C double bond (Cu-C 275.1 and 272.9 pm). The molecular geometries of the tri(1-cyclohepta-2,4,6-trienyl) complexes **2a** and **3a** are compared with those of the known tri(cyclohexyl)phosphane complexes, $(hfac)Cu[P(C_6H_{11})_3]_n$ ($n = 1$ (**2b**) and 2 (**3b**)), and related compounds.

*Key words:* Copper(I), 1,3-Diketonate Complexes, Olefinic Phosphanes, Crystal Structure

## Introduction

Although the olefinic phosphane, tri(1-cyclohepta-2,4,6-trienyl)phosphane, $P(C_7H_7)_3$ (**a**), is basically a two-electron phosphane ligand in copper(I) complexes [1, 2], the central double bond of either one or two cyclohepta-2,4,6-trienyl substituents may act as additional support for the bonding to the metal in the solid state, if space is available in the coordination sphere. Thus, one (of the three) cyclohepta-2,4,6-trienyl rings of **a** approaches the metal *via* its central (4,5) C=C double bond in $\{Cu[P(C_7H_7)_3](CH_3CN)_2\}PF_6$ [1], whereas two (of the three) cyclohepta-2,4,6-trienyl rings of **a** come close to the copper atom in CuX $[P(C_7H_7)_3]$ (X = Cl (**1a**), Br) [2] and (considering one $P(C_7H_7)_3$ ligand) in $\{Cu[P(C_7H_7)_3]_2\}PF_6$ [1]. This leads to a distorted tetrahedral coordination sphere around Cu(I) in all these compounds in the solid state. However, according to the $^1H$ and $^{13}C$ NMR spectra, the three cyclohepta-2,4,6-trienyl substituents are equivalent in solution at room temperature and are assumed to be freely-pending, flexible organyl groups in these Cu(I) compounds in solution.

We have now tested these results by combining $P(C_7H_7)_3$ (**a**) with the fragment hexafluoroacetylacetonato copper, [(hfac)Cu], which has two empty coordination sites. The two new complexes, $(hfac)Cu[P(C_7H_7)_3]_n$ ($n = 1$ (**2a**) and 2 (**3a**)) can be compared with the corresponding complexes containing tri(cyclohexyl)phosphane (**b**), *i. e.* $(hfac)Cu[PCy_3]_n$ ($n = 1$ (**2b**) and 2 (**3b**)), the molecular structures of which had been determined earlier [3].
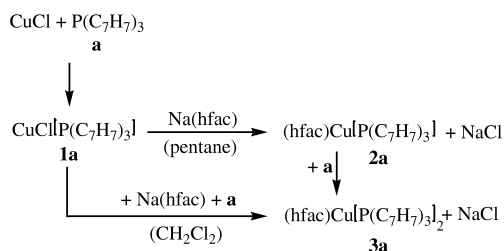
## Results and Discussion

$\beta$-Diketonato copper(I) complexes containing Lewis bases such as *tert*-phosphanes [3 – 6] or olefins [7, 8] have been investigated in detail. In the context of the search for volatile precursors for chemical vapour deposition (CVD) and generation of high-purity copper films [*cf.* 6, 9, 10, 11], a series of mononuclear hexafluoroacetylacetonato copper(I) complexes, $(hfac)Cu(L)$ (hfac= 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate; L = *tert*-phosphane, olefin or alkyne), has been prepared.

### Synthesis and spectroscopy

Complexes of *tert*-phosphanes with the fragment [(hfac)Cu] are either 1:1 adducts (hfac)Cu(L) (**2**) (L = $PMe_3$ [3, 4], $P^nBu_3$ [3], $PPh_3$ [3], $PCy_3$ [3]) or 1:2

adducts (hfac)Cu(L)$_2$ (**3**) (L = PMe$_3$ [3, 4], PPh$_3$ [3 – 5], PCy$_3$ [3, 12]). Both types may be formed simultaneously, and in solution the addition or elimination of the second *tert*-phosphane appears to be reversible [*cf.* 5]. The synthesis of the tri(1-cyclohepta-2,4,6-trienyl)phosphane copper(I) complexes **2a** and **3a** has been designed according to established routes for other copper(I) compounds with *tert*-phosphanes.

CuCl + P(C$_7$H$_7$)$_3$
**a**

CuCl[P(C$_7$H$_7$)$_3$] $\xrightarrow[\text{(pentane)}]{\text{Na(hfac)}}$ (hfac)Cu[P(C$_7$H$_7$)$_3$] + NaCl
**1a**                   **2a**

$\xrightarrow[\text{(CH}_2\text{Cl}_2)]{+ \text{Na(hfac)} + \textbf{a}}$ (hfac)Cu[P(C$_7$H$_7$)$_3$]$_2$ + NaCl
**3a**

The 1:1 complex **2a** is soluble in pentane and can therefore be extracted from the reaction mixtures and purified separately.

According to the $^1$H and $^{13}$C NMR spectra obtained for **2a** and **3a**, only one type of cyclohepta-2,4,6-trienyl substituents appears to be present in the CDCl$_3$ solutions at room temperature, and only one (slightly broadened) $^{31}$P NMR signal is found for both **2a** and **3a**. The $^{31}$P NMR signal is slightly shifted if additional ligand (**a**) is added to solutions of **2a**. These observations lead to the conclusion that the P(C$_7$H$_7$)$_3$ ligands in the 1:2 adduct **3a** are mobile in solution. Apparently, only one phosphane ligand remains firmly connected with the metal. This assumption is supported by the $^{31}$P NMR spectra of the silver complexes, (hfac)Ag[P(C$_7$H$_7$)$_3$]$_n$ ($n$ = 1, 2), analogous to **2a** and **3a**, which show the two well-resolved doublets, expected as a consequence of Ag-P spin-spin coupling ($\delta$ = −5.9, $^1J(^{109}$Ag,$^{31}$P) = 596 Hz and $^1J(^{107}$Ag,$^{31}$P) = 517 Hz in CD$_2$Cl$_2$ solution at 0 °C (*cf.* [2]).

The hexafluoroacetylacetonato (hfac) copper complexes have been studied preferentially (*cf.* [3, 4]) because they crystallize easily. The NMR signals of the fragment [(hfac)Cu] are unequivocally identified in the solutions of **2a** and **3a** in addition to those of the P(C$_7$H$_7$)$_3$ ligand, *e. g.* a singlet in the $^1$H NMR spectra at $\delta$(CH) *ca.* 5.8, and three signals in the $^{13}$C NMR spectra, *i. e.* a singlet at $\delta(^{13}$C) *ca.* 88 (CH) and two quartets near $\delta(^{13}$C) 117 (CF$_3$) ($^1J(^{19}$F,$^{13}$C *ca.* 290 Hz) and 176 (CO) ($^2J(^{19}$F,$^{13}$C) *ca.* 33 Hz). The $^1$H NMR data of the P(C$_7$H$_7$)$_3$ ligands (four signals

with an intensity ratio of 1:2:2:2) are similar to those of uncoordinated **a** [2, 18, 21], except that a broad absorption is observed at room temperature for the high-field signal corresponding to H$^1$. In the $^{13}$C NMR spectra (four signals) only the signal of C$^1$ appears as a doublet as a result of $^{31}$P,$^{13}$C spin-spin coupling, see Experimental Section.

### X-ray structure determinations of (hfac)Cu[P(C$_7$H$_7$)$_3$] (2a) and (hfac)Cu [P(C$_7$H$_7$)$_3$]$_2$ (3a)

The molecular geometries of **2a** and **3a** are shown in Figs 1 and 2; Tables 1 – 3 give interatomic distances and angles. Table 4 presents a comparison with the data for related hexafluoroacetylacetonate compounds such as the trimethylphosphane complex (hfac)Cu[PMe$_3$] [4], the tri(cyclohexyl)phosphane compounds (hfac)Cu[P(C$_6$H$_{11}$)$_3$]$_n$ ($n$ = 1 (**2b**) and
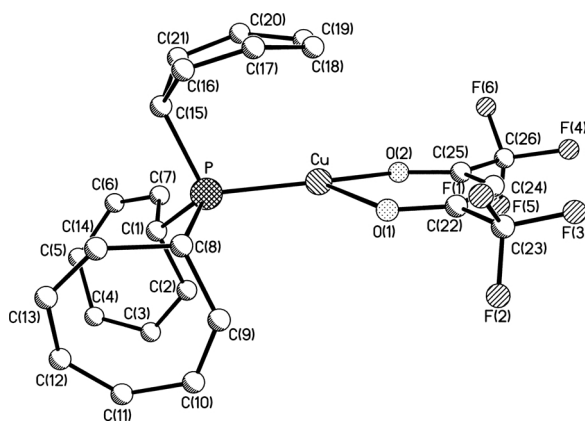


Fig. 1. Molecular structure of (hfac)Cu[P(C$_7$H$_7$)$_3$] (**2a**).
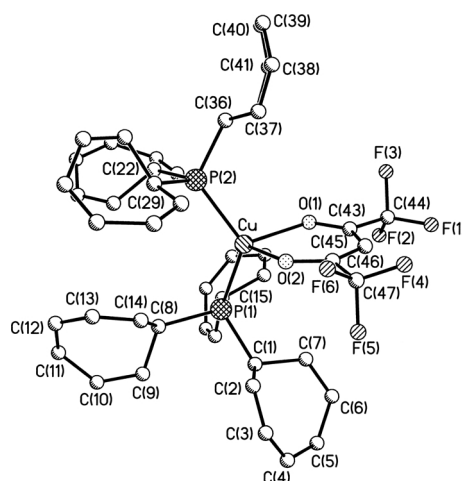


Fig. 2. Molecular structure of (hfac)Cu[P(C$_7$H$_7$)$_3$]$_2$ (**3a**).

Table 1. Bond lengths (pm) in (hfac)Cu[P(C₇H₇)₃] (**2a**).

| | | | |
|---|---|---|---|
| Cu-O(1) | 208.1(3) | P-C(1) | 181.8(4) |
| Cu-O(2) | 196.6(3) | P-C(8) | 184.2(5) |
| Cu-P | 214.3(1) | P-C(15) | 186.6(5) |
| C(1)-C(2) | 148.2(6) | C(8)-C(9) | 148.8(7) |
| C(1)-C(7) | 146.6(7) | C(8)-C(14) | 151.9(6) |
| C(2)-C(3) | 135.8(6) | C(9)-C(10) | 133.8(8) |
| C(3)-C(4) | 137.2(8) | C(10)-C(11) | 145.1(8) |
| C(4)-C(5) | 135.1(8) | C(11)-C(12) | 131.0(9) |
| C(5)-C(6) | 139.8(8) | C(12)-C(13) | 142.1(9) |
| C(6)-C(7) | 136.9(7) | C(13)-C(14) | 132.6(7) |
| C(15)-C(16) | 149.9(6) | F(1)-C(23) | 124.5(7) |
| C(15)-C(21) | 150.3(7) | F(2)-C(23) | 122.3(7) |
| C(16)-C(17) | 131.8(6) | F(3)-C(23) | 123.0(6) |
| C(17)-C(18) | 143.5(7) | F(4)-C(26) | 130.6(6) |
| C(18)-C(19) | 134.1(7) | F(5)-C(26) | 130.2(6) |
| C(19)-C(20) | 141.3(7) | F(6)-C(26) | 129.1(7) |
| C(20)-C(21) | 132.8(6) | C(22)-C(23) | 147.7(7) |
| | | C(22)-C(24) | 138.2(6) |
| O(1)-C(22) | 208.1(3) | C(24)-C(25) | 138.1(6) |
| O(2)-C(25) | 196.6(3) | C(25)-C(26) | 152.1(7) |

Table 2. Bond and dihedral angles (°) in (hfac)Cu[P(C₇H₇)₃] (**2a**).

*Bond angles:*

| | | | |
|---|---|---|---|
| O(1)-Cu-O(2) | 90.4(1) | C(1)-P-C(8) | 106.6(2) |
| P-Cu-O(1) | 116.2(1) | C(1)-P-C(15) | 103.9(2) |
| P-Cu-O(2) | 152.1(1) | C(8)-P-C(15) | 101.2(2) |
| Cu-P-C(1) | 121.6(3) | Cu-O(1)-C(22) | 123.1(3) |
| Cu-P-C(8) | 110.4(1) | Cu-O(2)-C(25) | 125.6(3) |
| Cu-P-C(15) | 111.1(1) | | |
| P-C(1)-C(2) | 115.2(3) | P-C(8)-C(9) | 110.9(3) |
| P-C(1)-C(7) | 116.8(3) | P-C(8)-C(14) | 115.9(3) |
| C(2)-C(1)-C(7) | 91.0(4) | C(9)-C(8)-C(14) | 114.1(4) |
| C(1)-C(2)-C(3) | 122.6(4) | C(8)-C(9)-C(10) | 129.1(5) |
| C(2)-C(3)-C(4) | 124.7(6) | C(9)-C(10)-C(11) | 127.3(6) |
| C(3)-C(4)-C(5) | 125.2(6) | C(10)-C(11)-C(12) | 127.7(6) |
| C(4)-C(5)-C(6) | 124.3(6) | C(11)-C(12)-C(13) | 127.1(6) |
| C(5)-C(6)-C(7) | 123.6(6) | C(12)-C(13)-C(14) | 129.9(6) |
| C(6)-C(7)-C(1) | 123.0(4) | C(13)-C(14)-C(8) | 127.1(5) |
| P-C(15)-C(16) | 111.0(3) | F(1)-C(23)-F(2) | 97.0(6) |
| P-C(15)-C(21) | 112.4(3) | F(1)-C(23)-F(3) | 101.1(6) |
| C(16)-C(15)-C(21) | 108.7(4) | F(2)-C(23)-F(3) | 104.9(7) |
| C(15)-C(16)-C(17) | 124.4(5) | F(1)-C(23)-C(22) | 115.1(6) |
| C(16)-C(17)-C(18) | 127.1(5) | F(2)-C(23)-C(22) | 115.2(5) |
| C(17)-C(18)-C(19) | 125.7(5) | F(3)-C(23)-C(22) | 120.2(5) |
| C(18)-C(19)-C(20) | 125.7(5) | | |
| C(19)-C(20)-C(21) | 127.4(5) | F(4)-C(26)-F(5) | 106.6(5) |
| C(20)-C(21)-C(15) | 125.0(5) | F(4)-C(26)-F(6) | 105.0(5) |
| O(1)-C(22)-C(23) | 114.5(4) | C(5)-C(26)-F(6) | 107.0(6) |
| O(1)-C(22)-C(24) | 127.8(4) | F(4)-C(26)-C(25) | 114.5(5) |
| C(23)-C(22)-C(24) | 117.7(4) | F(5)-C(26)-C(25) | 111.2(5) |
| C(22)-C(24)-C(25) | 124.0(4) | F(6)-C(26)-C(25) | 112.1(5) |
| O(2)-C(25)-C(24) | 128.2(4) | | |
| O(2)-C(25)-C(26) | 113.0(5) | | |
| C(24)-C(25)-C(26) | 118.8(4) | | |

*Dihedral angles[a]:*

| | | | |
|---|---|---|---|
| Cu-O(1)-O(2)/ Cu-(Z)-P | 84.9° | | |
| Substituents C₇H₇ | $\alpha_1$ 60.8; $\beta_1$ 20.3 | $\alpha_8$ 32.5; $\beta_8$ 16.8 | $\alpha_{15}$ 45.9; $\beta_{15}$ 23.1 |

[a] Z is the centre of the olefinic bond C(18)C(19). The dihedral angles $\alpha$ and $\beta$ (Fig. 3) refer to the bending of the cyclohepta-2,4,6-trienyl substituents which are attached to phosphorus *via* C(1), C(8) and C(15), respectively.

2 (**3b**)) [3], and the cycloocta-1,5-diene complex (hfac)Cu[C₈H₁₂] [8].

The bis(phosphane) complex **3a** (Fig. 2) posseses a symmetrical inner coordination core with almost equal Cu-O (212.0(3) and 212.7(3) pm) and Cu-P (224.9(1) and 223.8(1) pm) distances; the dihedral angle OCuO/PCuP is 89.1°. The long Cu-P distances come close to the corresponding Cu-P distances in the bis(tricyclohexylphosphane)copper(I) complexes (hfac)CuL₂ (**3b**) (227.7(3) and 225.1(3) pm [3]), (O₃Cl-O)CuL₂ (226.2(1) pm [12]) and (O-NO₂)CuL₂ (229(1) pm [13]). However, the angle P-Cu-P (123.9(1)° in **3a**) is considerably smaller than in the bis(tricyclohexylphosphane) analogues, (hfac)CuL₂ (**3b**) (141.3(1)° [3]), (O₃Cl-O)CuL₂ (144.5(1)° [12]) and (O-NO₂)CuL₂ (140(1)° [13]), L = P(C₆H₁₁)₃. The bulk of PCy₃ (**b**) as compared to P(C₇H₇)₃ (**a**) may also be estimated from the OCuO angles of 86.2(1)° in **3a** and 80.8(2)° in **3b** (see Table 4).

The coordination sphere of Cu(I) in the mono(phosphane) complex (hfac)Cu[P(C₇H₇)₃] (**2a**) (Fig. 1) can be classified – at least to a first approximation – as trigonal-planar; the Cu-P vector deviates by only 7.8° from the CuO(1)O(2) plane. However, the Cu atom protrudes by 12.0 pm out of the PO(1)O(2) plane, towards the olefinic double bond C(18)C(19). The distance between the metal and the centre (Z) of the C(18)C(19) bond (265.7 pm) may be taken to indicate a weak bonding interaction, as it had similarly been noticed in {Cu[P(C₇H₇)₃](CH₃CN)₂}PF₆ (Cu-Z 257.1(4) pm) and {Cu[P(C₇H₇)₃]₂}PF₆ (283.9
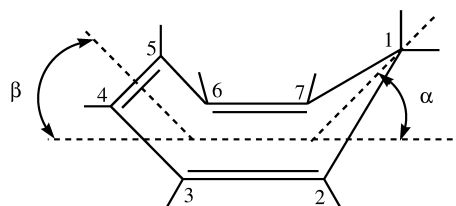


Fig. 3. Conformation of the 1-cyclohepta-2,4,6-trienyl substituent.

and 262.5 pm) [1], and in the halides CuX[P(C₇H₇)₃] (289.6 pm (X = Cl) and 284.3 pm (X = Br), respectively) [2]. Apparently the central double bond

Table 3. Selected bond lengths (pm) and angles (°) in (hfac)Cu[P(C$_7$H$_7$)$_3$]$_2$ (**3a**).

*Distances:*

| | | | |
|---|---|---|---|
| Cu-O(1) | 212.0(3) | Cu-O(2) | 212.7(3) |
| Cu-P(1) | 224.9(1) | Cu-P(2) | 223.8(1) |
| O(1)-C(43) | 123.6(5) | O(2)-C(46) | 124.0(4) |
| C(43)-C(45) | 138.3(6) | C(45)-C(46) | 139.0(5) |
| P(1)-C(1) | 184.6(4) | P(2)-C(22) | 184.7(4) |
| P(1)-C(8) | 185.4(4) | P(2)-C(29) | 185.0(3) |
| P(1)-C(15) | 184.5(4) | P(2)-C(36) | 184.5(3) |
| C(1)-C(2) | 149.6(6) | C(22)-C(23) | 150.4(5) |
| C(1)-C(7) | 148.1(7) | C(22)-C(28) | 150.1(5) |
| C(2)-C(3) | 135.1(7) | C(23)-C(24) | 133.3(7) |
| C(3)-C(4) | 142.8(10) | C(24)-C(25) | 143.6(9) |
| C(4)-C(5) | 134.5(10) | C(25)-C(26) | 132.9(9) |
| C(5)-C(6) | 142.0(10) | C(26)-C(27) | 141.2(8) |
| C(6)-C(7) | 133.8(7) | C(27)-C(28) | 132.8(6) |

*Angles:*

| | | | |
|---|---|---|---|
| O(1)-Cu-O(2) | 86.2(1) | P(1)-Cu-P(2) | 123.9(1) |
| Cu-P(1)-C(1) | 118.5(2) | Cu-P(2)-C(22) | 116.1(1) |
| Cu-P(1)-C(8) | 113.2(2) | Cu-P(2)-C(29) | 112.7(1) |
| Cu-P(1)-C(15) | 110.9(2) | Cu-P(2)-C(36) | 117.6(2) |
| C(1)-P(1)-C(8) | 104.8(2) | C(22)-P(2)-C(29) | 102.9(2) |
| C(1)-P(1)-C(15) | 104.8(2) | C(22)-P(2)-C(36) | 100.8(2) |
| C(8)-P(1)-C(15) | 103.0(2) | C(29)-P(2)-C(36) | 104.8(2) |
| P(1)-C(1)-C(2) | 112.8(3) | P(2)-C(22)-C(23) | 113.0(3) |
| P(1)-C(1)-C(7) | 114.3(3) | P(2)-C(22)-C(28) | 114.1(3) |
| C(2)-C(1)-C(7) | 104.7(4) | C(23)-C(22)-C(28) | 105.4(3) |
| C(1)-C(2)-C(3) | 119.7(5) | C(22)-C(23)-C(24) | 120.0(5) |
| C(2)-C(3)-C(4) | 123.6(6) | C(23)-C(24)-C(25) | 124.4(5) |
| C(3)-C(4)-C(5) | 126.1(6) | C(24)-C(25)-C(26) | 124.7(5) |
| C(4)-C(5)-C(6) | 125.5(6) | C(25)-C(26)-C(27) | 125.9(5) |
| C(5)-C(6)-C(7) | 124.1(6) | C(26)-C(27)-C(28) | 125.1(5) |
| C(6)-C(7)-C(1) | 120.5(5) | C(27)-C(28)-C(22) | 121.2(4) |

*Dihedral angles[a]:*

| | | | | | |
|---|---|---|---|---|---|
| CuO(1)O(2)/ CuP(1)P(2) | 89.1 | | | | |
| C$_7$H$_7$ Substituents | $\alpha_1$ 58.8 | | $\alpha_8$ 55.6 | | $\alpha_{15}$ 53.6 |
| | $\beta_1$ 27.4 | | $\beta_8$ 26.9 | | $\beta_{15}$ 26.9 |
| | $\alpha_{22}$ 55.6 | | $\alpha_{29}$ 53.8 | | $\alpha_{36}$ 58.4 |
| | $\beta_{22}$ 26.9 | | $\beta_{29}$ 26.4 | | $\beta_{36}$ 26.4 |

[a] The dihedral angles $\alpha$ and $\beta$ (Fig. 3) refer to the bending of the cyclohepta-2-4-6-trienyl substituents which are attached to P(1) *via* C(1), C(8), C(15) and to P(2) *via* C(22), C(29), C(36), respectively.

(C(18)C(19)) of one cyclohepta-2,4,6-trienyl substituent tends to occupy the fourth ligand position at the metal, although the basic trigonal coordination sphere is only slightly distorted. A comparable situation has been described for the cycloocta-1,5-diene complex, (hfac)Cu[C$_8$H$_{12}$], as a "3+1 coordination" with an asymmetrically coordinated cycloocta-1,5-diene ligand [8], where the distance of the metal to the centre (Z) of the "additional" double bond (241.8 pm) is considerably longer than that to the firmly attached olefinic bond (195.3 pm), (*cf.* Table 4); the distance between

Cu and the triple bond in the trigonal-planar diphenylacetylene compound, (hfac)Cu(C$_2$Ph$_2$), is 185.6 pm, with a dihedral angle (hfac)Cu/Cu(alkyne) of 2.2° [14]. In contrast to the $\pi$-complexes, (hfac)Cu(L) (L= cycloocta-1,5-diene [8], diphenylacetylene [14]), and to the bis(phosphane) complexes, (hfac)CuL$_2$ (L= P(C$_7$H$_7$)$_3$ (**3a**), PCy$_3$ (**3b**)), the mono(phosphane) compounds, (hfac)Cu(L) (L= PMe$_3$ [4], P(C$_7$H$_7$)$_3$ (**2a**), PCy$_3$ (**2b**)) show differing Cu-O distances (Table 1). The difference (Cu-O(1) 208.1(3) and Cu-O(2) 196.6(3) pm in **2a**) is particularly large, but the angle O(1)-Cu-O(2) (90.4 – 90.7°) is identical in all three mono(phosphane) compounds.

The structure of the ligand P(C$_7$H$_7$)$_3$ (**a**) in **2a**, in particular the slight deformation of the trigonal ligand sphere of copper(I) towards a pseudo-tetrahedral coordination, and the small but significant elongation of the double bond C(18)C(19) (134.1(7) pm) as compared with the double bonds in the same ring, C(16)C(17) (131.8(6) pm) and C(20)C(21) (132.8(6) pm), are all indications of a weak interaction between Cu(I) and the olefinic bond C(18)C(19). It is important to note, however, that the distances Cu⋯Z between the metal and the centre of the olefinic bond in the copper(I) complexes of tri(cyclohepta-2,4,6-trienyl)phosphane (250 – 290 pm [1, 2]) are considerably longer as compared with those in conventional Cu(I)-ethylene compounds (194 – 203 pm [15 – 17]); for discussions see also references [1, 2].

In the solid state, the cyclohepta-2,4,6-trienyl ring substituents (C$_7$H$_7$) of P(C$_7$H$_7$)$_3$ are always present in the boat conformation, both in all coordination compounds and in free P(C$_7$H$_7$)$_3$ (**a**) [18], and also in N(C$_7$H$_7$)$_3$ [19] and S(C$_7$H$_7$)$_2$ [20]. The extent of bending may be characterized by the magnitude of the dihedral angles $\alpha$ and $\beta$, as defined in Fig. 3. The 1:1 complex **2a** contains three C$_7$H$_7$ substituents which differ in their geometrical form in the crystal: the two free ring substituents carry the phosphorus atom either in an equatorial (at C(1)) or in an axial position (at C(8)). It is known [18 – 20] that axial cyclohepta-2,4,6-trienyl substituents are flatter than the equatorial counterparts, *i. e.* the dihedral angles $\alpha$ and $\beta$ are significantly smaller in the case of axial C$_7$H$_7$ rings. However, the loosely $\pi$-coordinated ring substituent – which has necessarily the axial connection at C(15) – assumes again a more bent geometry with $\alpha$ and $\beta$ angles larger than in the free axial ring (Table 2). On the other hand, all six cyclohepta-2,4,6-trienyl substituents in the 1:2 complex **3a** possess the equato-

| L = | (hfac)Cu(L) | | | (hfac)Cu($C_8H_{12}$) [8] | (hfac)Cu(L)$_2$ | | Table 4. Characteristic interatomic distances (pm) and angles (°) in hexafluoroacetylacetonato copper(I) complexes. |
|---|---|---|---|---|---|---|---|
| | PMe$_3$ [4] | PCy$_3$ (**2b**) [3] | P(C$_7$H$_7$)$_3$ (**2a**) | | P(C$_7$H$_7$)$_3$ (**3a**) | PCy$_3$ (**3b**) [3] | |
| Cu-P(1) | 214.2(3) | 215.2(2) | 214.3(1) | – | 224.9(1) | 225.1(3) | |
| Cu-P(2) | | | | | 223.8(1) | 227.7(3) | |
| Cu-Z(olefin) | – | – | 265.7 | 195.3 | – | – | |
| | | | | 241.8 | | | |
| Cu-C(olefin) | – | – | 272.9/275.1 | 204.9(6)/208.9(7) | – | – | |
| | | | | 246.6(8)/255.0(7) | | | |
| **hfac ligand** | | | | | | | |
| Cu-O(1) | 199.0(8) | 198.7(4) | 196.6(3) | 199.9(6) | 212.0(3) | 221.3(5) | |
| Cu-O(2) | 203.4(7) | 202.6(4) | 208.1(3) | 200.1(4) | 212.7(3) | 225.1(5) | |
| Cu-O(1)-C | 125.8(8) | 125.8(4) | 123.1(3) | 122.6(5) | 125.7(2) | 128.6(4) | |
| Cu-O(2)-C | 124.0(7) | 124.8(4) | 125.6(3) | 122.4(5) | 125.9(2) | 128.6(4) | |
| C-C-C (internal) | 124(1) | 123.8(6) | 124.0(4) | 124.6(6) | 123.6(4) | 122.8(7) | |
| **Angles at Cu (Z is the centre of the olefinic bond)** | | | | | | | |
| O(1)-Cu-O(2) | 90.5(3) | 90.7(2) | 90.40(12) | 93.3(2) | 86.19(10) | 80.8(2) | |
| P(1)-Cu-P(2) | – | – | – | – | 123.93(4) | 141.3(1) | |
| Z-Cu-Z | | | | 86.2 | | | |
| P(1)-Cu-O(1) | 140.2(2) | 139.6(1) | 116.19(9) | – | 107.91(8) | 112.4(2) | |
| P(1)-Cu-O(2) | 129.5(2) | 129.5(1) | 152.11(10) | – | 111.35(8) | 96.2(2) | |
| P(2)-Cu-O(1) | | | | | 109.77(8) | 95.7(2) | |
| P(2)-Cu-O(2) | | | | | 111.12(8) | 114.8(2) | |
| Z-Cu-O(1) | | | 98.0 | | | | |
| Z-Cu-O(2) | | | 94.5 | | | | |
| Z-Cu-P(1) | | | 90.2 | | | | |

rial arrangement with typical "equatorial" angles of $\alpha = 53 - 58°$ and $\beta = 26 - 28°$ (Table 3). It is interesting to note that uncoordinated P(C$_7$H$_7$)$_3$ (**a**) as well as [P(C$_7$H$_7$)$_4$]BF$_4$ both contain two equatorial substituents in the crystal [18], whereas all three C$_7$H$_7$ substituents in N(C$_7$H$_7$)$_3$ are equatorial [19] and both C$_7$H$_7$ substituents in S(C$_7$H$_7$)$_2$ are axial [20]. Apparently the cyclohepta-2,4,6-trienyl substituents are able to adapt their conformation to the space which is available in the crystal.

## Experimental Section

The reactions were routinely carried out under argon in dry, deoxygenated solvents. The synthesis of the starting compounds, P(C$_7$H$_7$)$_3$ (**a**) [18] and CuCl[P(C$_7$H$_7$)$_3$] (**1a**) [2] has been described; sodium hexafluoroacetylacetonate, Na(hfac), was a commercial product (Aldrich).

Instrumentation: NMR spectra: Bruker ARX 250; IR spectra: Perkin-Elmer 983 G.

### (hfac)Cu[P(C$_7$H$_7$)$_3$] (**2a**)

Pentane (30 ml) was added to an equimolar mixture of Na(hfac) (115 mg, 0.5 mmol) and CuCl[P(C$_7$H$_7$)$_3$] (**1a**) (202 mg, 0.5 mmol). The suspension was stirred at ambient temperature for 40 h. The yellow solution (containing the product **2a**) was then removed by needle-filtration and brought to dryness. The residue was redissolved in pentane (10 ml). Crystallization at −25 °C gave orange, air stable crystals. m. p. 97 °C, yield 210 mg (73%).

$^1$H NMR (250 MHz, CDCl$_3$); P(C$_7$H$_7$)$_3$ ligand: $\delta = 2.64$ (broad, 3H, H$^1$), 5.17 (m, 6H, H$^{2,7}$), 6.24 (m, 6H, H$^{3,6}$), 6.53 (m, 6H, H$^{4,5}$); hfac ligand: 5.87 (s, 1H). – $^{13}$C{$^1$H} NMR (62.9 MHz, CDCl$_3$); P(C$_7$H$_7$)$_3$ ligand: $\delta = 35.1$ (d, $^1J(^{31}P^{13}C) = 21.3$ Hz, C$^1$), 114.3 (C$^{2,7}$), 127.8 (C$^{3,6}$), 130.3 (C$^{4,5}$); hfac ligand: 88.0 (*C*H), 117.7 (q, $^1J(^{19}F,$ $^{13}C) = 287$ Hz, *C*F$_3$), 176.6 (q, $^2J(^{19}F,$ $^{13}C) = 33.3$ Hz, *C*O). – $^{31}$P NMR (101.3 MHz, CDCl$_3$): $\delta = -4.4$.

### (hfac)Cu[P(C$_7$H$_7$)$_3$]$_2$ (**3a**)

a) A suspension of Na(hfac) (220 mg, 0.956 mmol) in 5 ml of pentane was added to a stirred suspension of CuCl[P(C$_7$H$_7$)$_3$] (**1a**) (310 mg, 0.769 mmol) in 10 ml of pentane, and the yellow reaction mixture was stirred at 25 °C for 2 h. The pentane solution was removed (through a pipet) and discarded. The residue was dried under high-vacuum, then dissolved in THF, the solution filtered over Na$_2$SO$_4$ and the filtrate brought to dryness. m. p.: 91 °C, yield 180 mg (53.2%). Crystallization from CH$_2$Cl$_2$ at room temperature (under slow evaporation of the solvent) gave single crystals of **3a** which were suitable for X-ray structure analysis.

b) An equimolar mixture of 202 mg (0.5 mmol) of CuCl[P(C$_7$H$_7$)$_3$] (**1a**), 115 mg (0.5 mmol) of Na(hfac) and 152 mg (0.5 mmol) of P(C$_7$H$_7$)$_3$ (**a**) was stirred together with

Table 5. Crystallographic data and details of the structure refinement.

| | (hfac)Cu[P(C$_7$H$_7$)$_3$] (2a) | (hfac)Cu[P(C$_7$H$_7$)$_3$]$_2$ (3a) |
|---|---|---|
| Empirical formula | C$_{26}$H$_{22}$CuF$_6$O$_2$P | C$_{47}$H$_{43}$CuF$_6$O$_2$P$_2$ |
| Formula mass | 574.95 | 879.29 |
| Crystal | orange prism | yellow plate |
| Dimensions [mm] | $0.20 \times 0.17 \times 0.12$ | $0.35 \times 0.28 \times 0.09$ |
| Crystal system | monoclinic | triclinic |
| Space group | $P2_1/c$ | $P\bar{1}$ |
| Unit cell dimensions [pm, °] | $a = 1278.3(3)$ | $a = 1063.00(11)$ |
| | $b = 921.8(2)$ | $b = 1312.81(14)$ |
| | $c = 2186.3(4)$ | $c = 1652.89(13)$ |
| | | $\alpha = 95.342(6)$ |
| | $\beta = 101.21(3)$ | $\beta = 95.484(7)$ |
| | | $\gamma = 107.755(9)$ |
| Volume [pm$^3$] | $2527.0(9) \times 10^6$ | $2168.5(4) \times 10^6$ |
| Z | 4 | 2 |
| Density (calc.) g/cm$^3$ | 1.511 | 1.347 |
| Diffractometer | STOE IPDS I | Siemens P4 |
| Absorption coefficient [mm$^{-1}$] | 0.640 | 0.994 |
| F(000) | 1168 | 908 |
| Measuring range ($\theta$) | $2.25 - 28.15°$ | $1.64 - 22.50°$ |
| Index ranges | $-16 \leq h \leq 0$ | $-11 \leq h \leq 1$ |
| | $-11 \leq k \leq 0$ | $-13 \leq k \leq 13$ |
| | $-28 \leq l \leq 28$ | $-17 \leq l \leq 17$ |
| Reflections collected | 5791 | 6386 |
| Independent refls | 5791 | 5288 |
| | | [R(int.) = 0.0260] |
| Completeness | 93.7% | 93.1% |
| | up to $\theta = 28.15$ | up to $\theta = 22.50°$ |
| Absorption correction | none | none |
| Refinement method | – Full-matrix least-squares on $F^2$ – | |
| Refined parameters | 325 | 524 |
| Goodness-of-fit on $F^2$ | 0.670 | 1.090 |
| Final $R$ indices ($I > 2\sigma(I)$) | $R_1 = 0.0502$ | $R_1 = 0.0435$ |
| | $wR_2 = 0.1138$ | $wR_2 = 0.1149$ |
| $R$ Indices (all data) | $R_1 = 0.1292$ | $R_1 = 0.0521$ |
| | $wR_2 = 0.1298$ | $wR_2 = 0.1282$ |
| Extinction coefficient | – | 0.0126(11) |
| Max./min. residual electron density [e pm$^{-3} \times 10^{-6}$] | $0.679/-0.408$ | $0.579/-0.506$ |

30 ml of pentane for 40 h at room temperature. The yellow reaction mixture was then brought to dryness and the residue dissolved in CH$_2$Cl$_2$. Crystallization at $-25$ °C gave yellow crystals in nearly quantitative yield (400 mg, 91%).

$^1$H NMR (250 MHz, CDCl$_3$); P(C$_7$H$_7$)$_3$ ligands: $\delta = 2.10$ (broad, 6H, H$^1$), 5.20 (pseudo-triplet, 12 H, H$^{2,7}$), 6.22 (m, 12 H, H$^{3,6}$), 6.56 (m, 12 H, H$^{4,5}$); hfac ligand: $\delta = 5.69$ (s, 1H). – $^{13}$C{$^1$H} NMR (62.9 MHz, CDCl$_3$); P(C$_7$H$_7$)$_3$ ligands: $\delta = 34.3$ (d, $^1$J($^{31}$P,$^{13}$C) = 16.4 Hz, C$^1$), 115.1 (C$^{2,7}$), 126.8 (C$^{3,6}$), 130.5 (C$^{4,5}$); hfac ligand: $\delta = 87.4$ (CH), 117.6 (q, $^1$J($^{19}$F,$^{13}$C) = ca. 300 Hz, CF$_3$), 176.7 (q, $^2$J($^{19}$F,$^{13}$C) = 33.8 Hz, CO). – $^{31}$P NMR (101.3 MHz, CDCl$_3$): $\delta = -4.0 \pm 2$.

*Crystal structure determinations*

The crystallographic data and details concerning the structure refinement are presented in Table 5. The intensity data were collected at room temperature. The radiation used was Mo-K$_\alpha$ ($\lambda = 71.073$ pm), monochromatised by a graphite monochromator. All hydrogen atoms were refined on calculated positions, applying the riding model with fixed isotropic displacement parameters. The non-hydrogen atoms were refined with anisotropic displacement parameters.

The complete set of structural informations (excluding structure factors) for the structures reported in the present paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no CCDC-239940 (2a) and CCDC-239939 (3a).

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