Reactions and Coordination Properties of the First Secondary Carbaboranyldiphosphane: 1,2-Bis(phenylphosphanyl)-1,2-dicarba-*closo*-dodecaborane(12)☆

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When a mixture of stereoisomers of *rac*- and *meso*-1,2-bis(phenylphosphanyl)-1,2-dicarba-*closo*-dodecaborane(12) (**1a**, **b**; **1a**/**1b** = 3:1) is treated with [Cp_2ZrMe_2] in boiling toluene for 2 h, the formation of three phosphorus-containing products, namely *meso*-[$Cp_2Zr(PPh)_3$] (**3**), $(PPh)_4$ (**4**) and $(PPh)_5$ (**5**), ratio 2.8:1.1:1.0, was observed by ^{31}P-NMR spectroscopy. In the ^{11}B-NMR spectrum of the reaction mixture, only signals for 1,2-dicarba-*closo*-dodecaborane(12) were observed. When zirconocene, prepared in situ from [Cp_2ZrCl_2] and BuLi, was treated with **1a**, **b** at low temperature and then heated to reflux in toluene for 2 h, only formation of **3** and 1,2-dicarba-*closo*-dodecaborane(12) was observed. The mixture of stereoisomers of **1a**, **b** reacts with CuCl in THF to give *rac*- and *meso*-[CuCl(THF){1,2-$(PHPh)_2C_2B_{10}H_{10}$}] (**7a**, **b**), which is only stable in THF solution and loses THF in vacuo over several hours to yield the insoluble colorless complex [CuCl{1,2-$(PHPh)_2C_2B_{10}H_{10}$}]$_n$ (**8**). In THF solution, **7** reacts with PPh_3 to give the stable isolable complex [$CuCl(PPh_3)${1,2-$(PHPh)_2C_2B_{10}H_{10}$}] (**9**). No reaction of **1a**, **b** is observed with [$Cp'Mo(CO)_3]_2$ (Cp′ = C_5H_4Me) in boiling THF, while only decomposition occurs in boiling toluene. However, [$(NBD)Mo(CO)_4$] (NBD = norbornadiene) reacts smoothly with **1a** in toluene at room temperature to give *cis*-*rac*-[$Mo(CO)_4${1,2-$(PHPh)_2C_2B_{10}H_{10}$}] (**10**). Compounds **7**, **9**, and **10** were characterized spectroscopically (^1H, ^{31}P, ^{11}B, ^{13}C NMR, IR), and an X-ray structure determination was carried out on **10**.

Organo-element and organic derivatives of dicarba-*closo*-dodecaboranes(12) have received increasing attention during the last decade due to their interesting chemical and physical properties. Thus, these compounds have been employed as catalysts[1][2], as doping reagents in semiconductor materials[3], as precursors for ceramic materials[4], and in medical areas[5][6][7]. Hence applications in medicine can be envisioned for related carbaboranylphosphanes and their transition-metal complexes[8].

While tertiary phosphanyl derivatives of dicarba-*closo*-dodecaboranes(12), which were first reported in 1963[9], have been employed as ligands in transition-metal chemistry and as starting materials for the preparation of other *closo*-carbaborane(12)-containing organophosphorus compounds[10], their secondary analogues have remained largely unexplored[11]. We have recently reported the synthesis and spectroscopic properties of the first secondary bis(phosphanyl)carbaboranes, *rac*- and *meso*-1,2-bis(phenylphosphanyl)-1,2-dicarba-*closo*-dodecaborane(12) (**1a**, **1b**), as well as the molecular structure of the *rac* isomer **1a**[12].

We now report reactions and coordination properties of **1a**, **b** towards transition-metal complexes.

Results and Discussion

Reactions of 1,2-Bis(phenylphosphanyl)-1,2-dicarba-*closo*-dodecaborane(12) (1)

We have studied the reaction of a mixture of stereoisomers of *rac*- and *meso*-1,2-bis(phenylphosphanyl)-1,2-dicarba-*closo*-dodecaborane(12) [**1** (mixture of stereoisomers), **1a** (*rac*), **1b** (*meso*)][12] with various transition-metal complexes, i.e., [Cp_2ZrMe_2] (Cp = C_5H_5), [Cp_2ZrCl_2]/BuLi, CuCl, [$Cp'Mo(CO)_3]_2$ (Cp′ = C_5H_4Me) and [$(NBD)Mo(CO)_4$] (NBD = norbornadiene) (Scheme 1). As already observed in the reaction of **1** with sulfur[12], the chemical reactivity of **1** differs markedly from that of comparable carbaboranyldiphosphanes with tertiary phosphanyl groups or alkyl- or aryl-substituted secondary diphosphanes. In the case of dimethylzirconocene, the course of reaction is similar to that observed with the primary phosphane $PhPH_2$[13].

Reaction of 1a, b with Dimethylzirconocene or Zirconocene

When a mixture of stereoisomers of **1** (**1a**/**1b** = 3:1) was treated with dimethylzirconocene in boiling toluene for 2 h (Scheme 1), the formation of three phosphorus-containing products − *meso*-[$Cp_2Zr(PPh)_3$] (**3**)[13][14], $(PPh)_4$ (**4**)[15], and $(PPh)_5$ (**5**)[16] (ratio 2.8:1.1:1.0) − was observed by ^{31}P-NMR spectroscopy. The ^1H-NMR spectrum of the reaction mixture showed the presence of unreacted dimethylzirconocene (ca. 75%). **3** was isolated in 23% yield (based on reacted dimethylzirconocene) and characterized by comparison of its NMR data with those reported in the literature[13][14]. In the ^{11}B-NMR spectrum of the reaction mixture, only signals for 1,2-dicarba-*closo*-dodecaborane(12) were observed. As **1** exhibits remarkable thermal stability (up to 195°C in undecane solution), the formation of the

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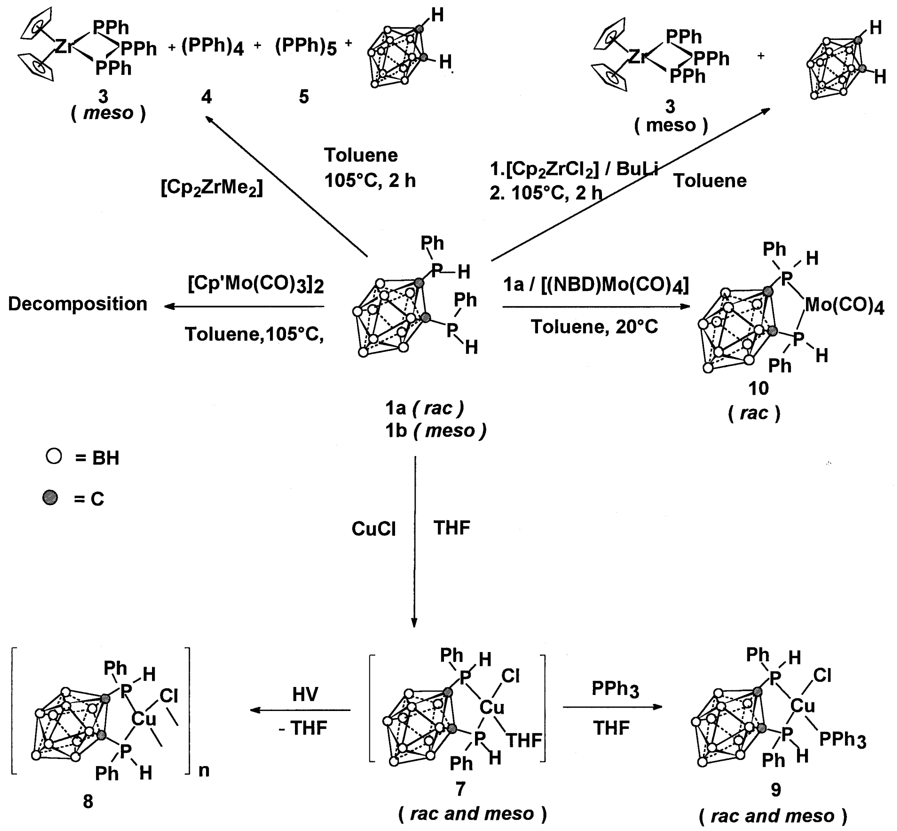
Scheme 1



observed products **3**−**5** and 1,2-dicarba-*closo*-dodecaborane(12) must be due to reaction with dimethylzirconocene rather than decomposition of **1**.

When a mixture of stereoisomers of **1** (**1a**/**1b** = 3:1) is treated with "zirconocene", prepared in situ from [Cp_2ZrCl_2] and BuLi by the Negishi method[17], followed by 2 h reflux in toluene, formation of **3** and 1,2-dicarba-*closo*-dodecaborane(12) is observed (Scheme 1); the cyclooligophosphanes **4** and **5** are not formed. The course of the reaction was monitored by ^{31}P-NMR spectroscopy. At room temperature, the spectrum of the burgundy red solution exhibits two major resonances at $\delta = -2.0$ ($^1J_{PH}$ = 233 Hz) and $\delta = -2.6$ ($^1J_{PH}$ = 230 Hz), which may be due to the *rac* and *meso* isomers of the intermediate [$Cp_2Zr\{1,2\text{-}(PHPh)_2C_2B_{10}H_{10}\}$] (**6**). On heating the solution to reflux for 2 h, the signals corresponding to **6** are replaced by those of **3** and two low-intensity signals at $\delta = -24$ and $\delta = -31$ from an as yet unknown compound. Apparently, **6** decomposes with elimination of 1,2-dicarba-*closo*-dodecaborane(12) and formation of **3** as the final product.

The fact that **4** and **5** are not formed suggests the involvement of a different intermediate in the reaction between dimethylzirconocene and **1** in refluxing toluene. A phosphanylidenezirconocene complex, which is the most likely intermediate, was not observed.

Reaction of 1a, b with Copper(I) Chloride

A mixture of stereoisomers of **1** (**1a**/**1b** = 3:1) reacts with copper(I) chloride in THF over 1 h to give a yellow solution, which we believe contains the THF adduct *rac*- and *meso*-[$CuCl(THF)\{1,2\text{-}(PHPh)_2C_2B_{10}H_{10}\}$] (**7**) (Scheme 1, Table 1), based on NMR studies. **7** is only stable in THF solution and as a solid loses THF in vacuo over several hours to yield the insoluble colorless complex [$CuCl\{1,2\text{-}(PHPh)_2C_2B_{10}H_{10}\}]_n$ (**8**). The latter is comparable to [$CuCl\{1,2\text{-}(PPh_2)_2C_2B_{10}H_{10}\}$][18], which was obtained from $CuCl_2$ and 1,2-bis(diphenylphosphanyl)-1,2-dicarba-*closo*-dodecaborane(12). In THF solution, **7** reacts with PPh_3 to give the stable isolable complex [$CuCl(PPh_3)\{1,2\text{-}(PHPh)_2C_2B_{10}H_{10}\}$] (**9**) in 92% yield (Scheme 1). **9** is soluble in THF and toluene. In the ^{31}P-NMR spectrum, only two broad signals are observed for coordinated PPh_3 and **1**, and this is due to the quadrupole moment of Cu. In the ^{1}H-NMR spectrum, signals for the P−H protons and the phenyl (PH*Ph* and P*Ph*$_3$) ligands are observed in the ratio 2:10:15. In contrast to complex **7** and the free ligand **1**, signals corresponding to *rac*- and *meso*-**9** were not observed. In the ^{13}C-NMR spectrum, the C atoms of the carborane cluster appear as a multiplet at $\delta = 81.3$. Signals corresponding to coordinated PPh_3 are observed in the us-

Table 1. NMR (^{31}P, ^{1}H, ^{13}C, ^{11}B) and IR data of compounds **1a**, **b**[12] (NMR in C_6D_6), **7** (NMR in [D_8]THF), **9** (NMR in C_6D_6) and **10** (NMR in C_6D_6)

	δ $^{31}P/J$ [Hz]	δ $^{1}H/J$ [Hz]	δ $^{13}C/J$ [Hz]	δ $^{11}B/^{1}J_{BH}$ [Hz]	ṽ [cm^{-1}] in KBr
1a	−15.15/246 ($^{1}J_{PH}$), 84 ($^{3}J_{PP}$)	7.30 m, 7.00 m (Ph), 4.78/244 ($^{1}J_{PH}$), 82 ($^{3}J_{PP}$) (PH), 3.5−1.6 br. m (B−H)	136.8 m, 131.0, 130.9, 129.0 (Ph), 76.3 m ($C_2B_{10}H_{10}$)	−0.9/142, −7.2/144, −9.4/225, −11.3	2626, 2606, 2583, 2561 (BH); 2323 (PH)
1b	−14.98/239 ($^{1}J_{PH}$), 87 ($^{3}J_{PP}$)	7.30 m, 7.00 m (Ph), 4.78/239 ($^{1}J_{PH}$), 87 ($^{3}J_{PP}$) (PH), 3.5−1.6 br. m (B−H)	136.8 m, 131.0, 130.9, 129.0 (Ph), 77.6 m ($C_2B_{10}H_{10}$)	−0.9/142, −7.2/144, −9.4/225, −11.3	2626, 2606, 2583, 2561 (BH); 2323(PH)
7	−14.5 v br.	7.76 m (**7a**), 7.53 m (**7b**), 7.41 m (Ph); 5.50/341 ($^{1}J_{PH}$), 172 ($^{3}J_{PP}$) (PH) (**7a**), 5.45/339 ($^{1}J_{PH}$), 179 ($^{3}J_{PP}$) (PH) (**7b**); 3.5−1.6 br. m (B−H)		−2.1, −5.4, −9.8	
9	1.08, −7.95/316 ($^{1}J_{PH}$)	8.23 br. m, 7.72 br. m, 7.05 m, 6.95 m (Ph), 5.12/320 ($^{1}J_{PH}$), 107 ($^{3}J_{PP}$) (PH), 3.5−1.6 br. m (B−H)	137.6 br. m, 134.75[a]/14.6 ($^{1}J_{CP}$), 133.0, 130.9[a], 130.1, 129.7[a], 129.6[a] (Ph), 81.3 m ($C_2B_{10}H_{10}$)	−1.6, −4.1, −9.1	2581 (BH); 2338 (PH)
10	67.70/358 ($^{1}J_{PH}$)	7.40 m, 6.97 m (Ph), 6.08/358 ($^{1}J_{PH}$), 19 ($^{2}J_{PP}$) (PH), 3.5−1.6 br. m (B−H)	212.3/9.9[b], 209.2/9.2[b] (CO), 134.7 m, 133.2, 130.1 m (Ph), 82.8 m ($C_2B_{10}H_{10}$)	−2.6/165, −3.9/151, −8.9, −11.4, −13.1	2593 (BH); 2034, 1955, 1936, 1905 (CO); 2342 (PH)

[a] PPh_3. − [b] Observed splitting in virtual triplet.

ual range for PPh_3−CuCl complexes[18][19] (Table 1). Molecular-mass determination with a vapor-pressure osmometer showed **9** to be monomeric in solution (calcd. 722, found 724). In conclusion, the data given are in agreement with a tetrahedral structure for **9**, in which the bis(phosphanyl)carbaborane is coordinated in a chelating fashion (Scheme 1). According to the NMR data (Table 1), the THF adduct **7** has a similar structure. Due to the low solubility of **8**, attempts to determine the molecular structure in solution were unsuccessful. A comparison with the CuCl complexes [CuCl{1,2-$(PPh_2)_2C_2B_{10}H_{10}$}][18] and [CuCl{1-$(PPh_2)C_2B_{10}H_{11}$}$_2$]$_n$[20] suggests an oligomeric structure.

Reaction of 1a, b with Carbonylmolybdenum Complexes

The reaction of **1a**, **b** with carbonylmolybdenum complexes depends on the nature of the Mo complex employed (Scheme 1). Thus, in contrast to primary and secondary alkyl- and arylphosphanes[21], no reaction is observed with [Cp′Mo(CO)$_3$]$_2$ (Cp′ = C_5H_4Me) in boiling THF. In boiling toluene reaction did occur, but a complex mixture of products was formed that could not be separated, isolated, or characterized.

However, [(NBD)Mo(CO)$_4$] reacts smoothly with **1a** in toluene at room temperature to give *cis*-*rac*-[Mo(CO)$_4${1,2-$(PHPh)_2C_2B_{10}H_{10}$}] (**10**; Scheme 1) in 73% yield. In the solid state, **10** is air- and moisture-stable. In solution, however, **10** slowly decomposes on exposure to air.

Molecular Structure of *cis-rac*-[Mo(CO)$_4${1,2-$(PHPh)_2C_2B_{10}H_{10}$}] (10)

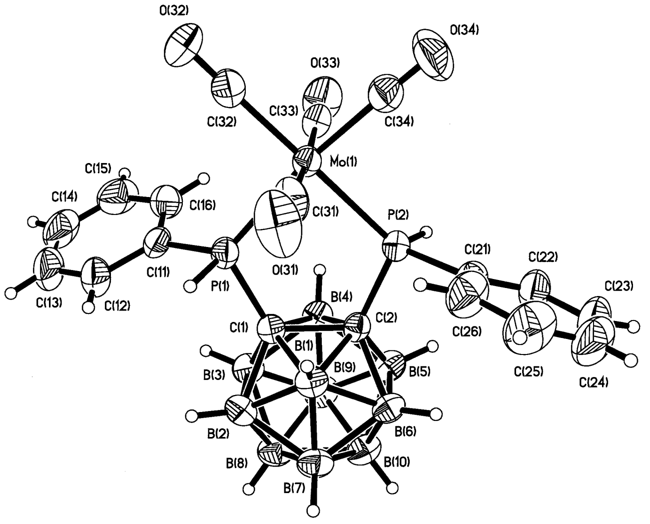
Single crystals of **10** were obtained from toluene/hexane solution at −5°C. **10** crystallizes in the centrosymmetric space group $P2_1/c$. The X-ray structure determination (Figure 1) shows that both enantiomers of the racemic isomer are present in the unit cell. The bis(phosphanyl)carbaborane is coordinated in a chelating fashion. The structural parameters of **1a**[12] remain almost unchanged on coordination to the Mo atom [$C_{cluster}$−$C_{cluster}$ 1.683(2) (**1a**), 1.681(3) Å (**10**); P−$C_{cluster}$ 1.8727(13) (**1a**), 1.873(2), 1.872(2) Å (**10**); P−C_{Ph} 1.8244(14) (**1a**), 1.815(2), 1.813(2) Å (**10**)]. A comparison of **10** with *cis*-tetracarbonyl{1,4-η^2-[1,2-dimethyl-1,2-bis(phenylphosphanyl)disilane]}molybdenum(0) (*cis-rac*-**11**)[22], the only other structurally characterized complex of an Mo(CO)$_4$ fragment with a coordinated secondary diphosphane ligand (Figure 2), shows that the Mo−P bond lengths [2.4445(6), 2.4559(6) Å (**10**); 2.550(1) Å (**11**)] and P−Mo−P bond angle [84.31(2) (**10**); 89.4(1)° (**11**)] of **10** are smaller.

For the Mo−CO groups *trans* to the coordinated P atoms, the Mo−C distances are larger [2.015(3), 2.017(3)Å (**10**); 1.994(4) Å (**11**)] and the C−O bond lengths shorter [1.139(3), 1.140(3)Å (**10**); 1.152(5) Å (**11**)] in **10**. Similar trends, that is, lengthening of the Mo−P and C−O bonds and shortening of the Mo−C bonds, are observed for the complexes [Mo(CO)$_4$(PMePhR)$_2$] (R = Me, Ph)[23], [Mo(CO)$_4${1,2-$(PPh_2)_2C_2H_4$}][24] and [Mo(CO)$_4${1,2-$(PPh_2)_2C_2H_2$}][25] (Table 2), which are similar to **11**. This suggests increased π-acceptor properties of the P atoms in **1a**, in comparison with other phenyl-substituted phosphanes or diphosphanes[29], due to the presence of the electron-deficient carbaboranyl ligand in **1a**[30]. Accordingly, in the IR spectrum the CO vibrations of **10** are shifted to higher wavenumbers by 10−20 cm^{-1} compared with other tetracarbonyl(diphosphane)- or -bis(phosphane)molybdenum complexes[26][27][28] (Table 2).

Discussion of ^{31}P- and ^{1}H-NMR Data of 1, 7, 9, and 10

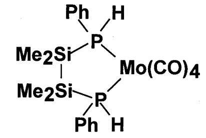
The mixture of stereoisomers of **1a**, **b** exhibits ^{31}P- and ^{1}H-NMR spectra in which the signals of the *HP*−CC−*PH* group appear as multiplets corresponding to an AA′XX′ spin system[12]. Simulation of the ^{1}H-NMR spectra allowed the corresponding coupling constants to be calculated [**1a**: $^{1}J_{PH}$ = 244 Hz, $^{3}J_{PP}$ = 84 Hz; **1b**: $^{1}J_{PH}$ = 239 Hz, $^{3}J_{PP}$ = 87 Hz][31]. Similar coupling patterns were observed in the ^{1}H-NMR spectra of **7**, **9** and **10**. The P-P coupling of the P−C−C−P fragment was observed only in the ^{1}H-NMR

Figure 1. Molecular structure of *cis-rac*-$[Mo(CO)_4\{1,2\text{-}(PHPh)_2C_2B_{10}H_{10}\}]$ (**10**); only one of the present enantiomers (*R*,*R*) with its atom-numbering scheme is shown (SHELXTL PLUS; XP)[37][a]



[a]Selected bond lengths [Å] and bond angles [°]: Mo(1)−P(1) 2.4559(6), Mo(1)−P(2) 2.4445(6), Mo(1)−C(31) 2.036(3), Mo(1)−C(32) 2.017(3), Mo(1)−C(33) 2.046(3), Mo(1)−C(34) 2.015(3), P(1)−C(11) 1.815(2), P(1)−C(1) 1.873(2), P(2)−C(21) 1.813(2), P(2)−C(2) 1.872(2), O(31)−C(31) 1.139(3), O(32)−C(32) 1.140(3), O(33)−C(33) 1.138(3), O(34)−C(34) 1.139(3), C(1)−C(2) 1.681(3); C(32)−Mo(1)−C(34) 92.85(11), C(31)−Mo(1)−C(34) 90.08(11), C(32)−Mo(1)−C(31) 88.67(12), C(33)−Mo(1)−C(34) 89.77(11), C(32)−Mo(1)−C(33) 87.80(11), C(31)−Mo(1)−C(33) 176.46(10), C(32)−Mo(1)−P(2) 175.00(9), C(34)−Mo(1)−P(1) 171.95(8), P(1)−Mo(1)−P(2) 84.31(2), Mo(1)−P(1)−C(1) 112.20(7), Mo(1)−P(2)−C(2) 112.56(7), C(11)−P(1)−C(1) 102.70(10), C(11)−P(1)−Mo(1) 127.10(8), C(1)−P(1)−Mo(1) 112.20(7), C(21)−P(2)−C(2) 102.06(10), C(21)−P(2)−Mo(1) 125.63(9), C(2)−P(2)−Mo(1) 112.56(7).

Figure 2. *cis*-Tetracarbonyl{1,4-η^2-[1,2-dimethyl-1,2-bis(phenylphosphanyl)disilane]}molybdenum(0)



***rac*-11**

spectra of **7** and **9**. For **10**, the coupling constant of the P−Mo−P fragment ($^2J_{PP}$ = 19 Hz) was observed in the ^1H-NMR spectrum[27]. However, due to line broadening in the proton-coupled ^{31}P-NMR spectra, only P-H coupling was observed for **9** and **10**, and for **7** only one broad signal ($\nu_{1/2} \approx 600$ Hz) was present. As expected, for all complexes the coupling constant $^1J_{PH}$ increases on coordination (Table 1).

Conclusions

The reaction of the recently reported 1,2-bis(phenylphosphanyl)-1,2-dicarba-*closo*-dodecaborane(12) (**1a, b**)[12] with several transition-metal complexes is dependent on the metal and the complex employed (Scheme 1). With electron-poor zirconocene derivatives, reactions similar to those of primary phosphanes are observed[13]. In contrast, the electron-rich compounds CuCl and $[(NBD)Mo(CO)_4]$ react with formation of the chelate complexes **7** and **10**, respectively. In vacuum **7** loses THF in the solid state and oligomerizes. With PPh_3, the stable monomeric complex **9** is obtained. In **10**, the carbaboranylbis(phosphane) ligand exhibits a higher π-acceptor ability compared to other diphosphanes in complexes of $Mo(CO)_4$, due to the presence of the electron-deficient carbaboranyl fragment.

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Experimental Section

All experiments were carried out under purified dry argon. Solvents were dried and freshly distilled under argon. − The NMR spectra were recorded with an AVANCE DRX 400 spectrometer (Bruker); ^1H NMR: internal standard solvent (benzene), external standard TMS; ^{13}C NMR: external standard TMS, internal standard solvent; ^{31}P NMR: external standard 85% H_3PO_4; ^{11}B NMR: external standard $BF_3 \cdot Et_2O$. − The IR spectra were recorded with an FT-IR spectrometer Perkin-Elmer System 2000 in the range of 350−4000 cm^{-1}. − Molecular-mass determination: Vapour Pressure Osmometer (Knauer), in $CHCl_3$ at 35°C. − X-ray structural analysis: Siemens SMART CCD diffractometer. − The melting points were determined in sealed capillaries under argon and are uncorrected. − $[Cp_2ZrMe_2]$[32], $[Cp_2ZrCl_2]$[33], $[Cp'Mo(CO)_3]_2$[34]

Table 2. Comparison of selected bond lengths and CO vibrations of compound **10** with those of other $Mo(CO)_4L_2$ complexes with phenyl-substituted diphosphane and bis(phosphane) ligands

L_2	Mo−P [Å]	Mo−C *trans* to P [Å]	C−O *trans* to P [Å]	Ref.	ν(CO) [cm^{-1}]	Ref.
1,2-$(PHPh)_2C_2B_{10}H_{10}$	2.4445(6), 2.4559(6)	2.017(3), 2.015(3)	1.139(3), 1.140(3)	this work	2036, 1940, 1934, 1897 (hexane) 2034, 1955, 1936, 1905 (KBr)	this work
$H(Ph)PSiMe_2SiMe_2P(Ph)H$	2.550(1)	1.994(4)	1.152(5)	[22]		
$Ph_2PCH_2CH_2PPh_2$	2.500(2), 2.495(2)	1.999(8), 1.974(8)	1.140(8), 1.164(9)	[24]	2021, 1929, 1919, 1903 (C_6H_{12}) 2020, 1919, 1907, 1881 ($C_2H_4Cl_2$)	[26]
$Ph_2PCH{=}CHPPh_2$	2.501(1), 2.494(1)	1.993(5), 1.976(5)	1.152(6), 1.138(7)	[25]		
$H(Ph)PCH_2CH_2P(Ph)H$					2023, 1928, 1908, 1892 (CH_2Cl_2)[a] 2023, 1927, 1908, 1893 (CH_2Cl_2)[b]	[27]
$(PPh_3)_2$	2.576(2), 2.577(2)	1.972(8), 1.973(9)	1.158(8), 1.149(8)	[23]	2023, 1927, 1908, 1897 ($C_2H_4Cl_2$)	[28]
$(PMePh_2)_2$	2.545(1), 2.565(1)	1.981(6), 1.975(6)	1.153(7), 1.152(7)	[23]	2020, 1925, 1902, 1891 ($C_2H_4Cl_2$)	[28]
$(PMe_2Ph)_2$	2.525(2), 2.533(2)	1.981(6), 1.983(6)	1.150(7), 1.163(7)	[23]	2018, 1920, 1900, 1891 ($C_2H_4Cl_2$)	[28]

[a] *rac* isomer. − [b] *meso* isomer.

and $[(NBD)Mo(CO)_4]$[35] were prepared by literature procedures. 1,2-Bis(phenylphosphanyl)-1,2-dicarba-*closo*-dodecaborane(12) (**1**) was prepared as described earlier[12]. CuCl and PPh_3 are commercially available.

Reaction of **1** *with Dimethylzirconocene:* A mixture of stereoisomers of **1** (1.2 g, 3.33 mmol, **1a**/**1b** = 3:1) and dimethylzirconocene (0.84 g, 3.35 mmol) were heated in toluene (20 ml) at 105°C for 2 h. After allowing the mixture to cool to room temperature, the solvent was distilled off. The resulting residue was characterized by ^1H-,^{11}B- and ^{31}P-NMR spectroscopy. *meso*-$[Cp_2Zr(PPh)_3]$ (**3**) was isolated by washing the residue with hexane and ether, and then dissolving it in toluene. Filtration and cooling the solution to −30°C gave 0.4 g of **3** (23% based on $[Cp_2ZrMe_2]$). The spectroscopic data of **3** are in agreement with those reported previously[13][14].

Reaction of **1** *with Zirconocene Dichloride/BuLi:* At −80°C, BuLi in hexane (2 equiv.) was added slowly to a suspension of $[Cp_2ZrCl_2]$ (0.29 g, 1.15 mmol) in toluene (10 ml) to generate "zirconocene" in situ. The mixture was stirred at −80°C for 1 h, then at −50°C for 15 min. The mixture was quickly brought to 20°C and a solution of **1** (0.35 g, 0.97 mmol, **1a**/**1b** = 3:1) in toluene (15 ml) was added. Samples for ^{11}B- and ^{31}P-NMR studies were taken after stirring the reaction mixture for 4 h at room temperature and for 2 h at 105°C.

Reaction of **1** *with CuCl. − [1,2-Bis(phenylphosphanyl)-1,2-dicarba-closo-dodecaborane(12)](tetrahydrofuran)copper(I) Chloride* (**7**) *and [1,2-Bis(phenylphosphanyl)-1,2-dicarba-closo-dodecaborane(12)]copper(I) Chloride* (**8**): A mixture of **1** (0.93 g, 2.58 mmol, **1a**/**1b** = 3:1) and CuCl (0.2 g, 2.22 mmol) in THF (25 ml) was stirred at room temperature for 1 h. The solvent was then removed from the clear yellow solution in vacuo to give a yellow solid (presumably the THF adduct **7**) which turned colorless after 2 h in vacuo, giving the final product **8**. The solid was washed with THF, toluene, and ether to give 0.78 g (76%) of **8**; dec. 267°C. − IR (KBr): $\tilde{\nu}$ = 3055 cm^{-1} (ν C−H), 2579 (ν B−H), 2350 (ν P−H). − $C_{14}H_{22}B_{10}ClCuP_2$ (459.39): calcd. C 36.60, H 4.83, Cl 7.72; found C 37.25, H 4.71, Cl 7.59. − **7** was characterized in $[D_8]$THF solution by ^{31}P-, ^1H- and ^{11}B-NMR spectroscopy (Table 1).

Reaction of **1** *with CuCl and* PPh_3. − *[1,2-Bis(phenylphosphanyl)-1,2-dicarba-closo-dodecaborane(12)](triphenylphosphane)copper(I) Chloride* (**9**): A mixture of **1** (0.7 g, 1.94 mmol, **1a**/**1b** = 3:1) and CuCl (0.19 g, 1.92 mmol) in THF (25 ml) was stirred at room temperature for 1 h. PPh_3 (0.5 g, 1.91 mmol) was added and the mixture stirred for 16 h. After filtration, the solvent was removed by distillation to give 1.28 g (92%) of **9** which can be recrystallized from THF/toluene; m.p. 218−219°C. − $C_{32}H_{37}B_{10}ClCuP_3$ (721.68): calcd. C 53.26, H 5.17, Cl 4.91; found C 53.55, H 5.17, Cl 5.59.

[1,2-Bis(phenylphosphanyl)-1,2-dicarba-closo-dodecaborane(12)]tetracarbonylmolybdenum(0) (**10**): A mixture of **1a** (0.7 g, 1.94 mmol) and $[(NBD)Mo(CO)_4]$ (0.6 g, 1.93 mmol) in toluene (30 ml) was stirred at room temperature for 20 h. The solvent was removed in vacuo and the resulting solid was recrystallized from toluene/hexane (20 ml/10 ml). At −5°C crystals of **10** were obtained. Yield 0.8 g (73%); dec. 252−254°C. − $C_{18}H_{22}B_{10}MoO_4P_2$ (568.34): calcd. C 38.04, H 3.90; found 38.70, H 4.18.

Data Collection and Structural Refinement of **10**[36]: Data (Mo-K_α, λ = 0.71073 Å) were collected with a Siemens CCD (SMART). All observed reflections (2Θ range: 2−52°) were used for determination of the unit-cell parameters. The structures were solved by direct methods (SHELXTL PLUS[37]) and subsequent difference Fourier syntheses, and refined by full-matrix least squares on F^2 (SHELXTL PLUS[37]). Mo, O, P, B, and C atoms refined anisotropically, H atoms located and refined isotropically. Empirical absorption correction with SADABS[38]. − Crystal data: $C_{18}H_{22}B_{10}MoO_4P_2$, M = 568.34, white crystals, 0.4 × 0.3 × 0.2 mm, monoclinic, space group $P2_1/c$ (no. 14), T = 293(2) K, a = 22.012(1), b = 6.8393(4), c = 18.657(1) Å, β = 111.978(1)°, V = 2604.7(3) $Å^3$, Z = 4, $D_{calcd.}$ = 1.449 Mg m^{-3}, $F(000)$ = 1136, μ(Mo-K_α) = 0.651 mm^{-1}, 11162 reflections collected with 1° < Θ < 26°; 4622 of these were independent; 404 parameters, *GOOF* = 1.100, residual electron density 0.321/−0.474 $Å^{-3}$, refinements converge to $R1$ = 0.0284, $wR2$ = 0.0734 [for reflections with $I > 2\sigma(I)$], $R1$ = 0.0335, $wR2$ = 0.0766 (all data).

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[36] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100919. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: int. code + (1223)336-033, e-mail: deposit@ccdc.cam.ac.uk).

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