Contributions to the Chemistry of Boron, 233[◇]

Reactions of a 1,2,3,4-Diphosphadiboretane with Some Carbonylmetal Compounds☆

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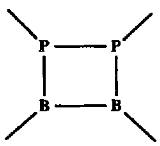
1,2-Di-*tert*-butyl-3-(diisopropylamino)-4-(dimethylamino)-1,2,3,4-diphosphadiboretane (**1**) reacts with $Fe_2(CO)_9$ to give two isomeric tetracarbonyliron complexes **2**, **3** with P–Fe bonds and a bis(tetracarbonyliron) complex **4**. In contrast, **1** displaces the olefinic ligand from tetracarbonyl(η^4-norbornadiene)metal (metal = Cr, Mo) to form the tetracarbonylmetal complexes **5** and **6** with a rearranged ligand molecule, i.e. a 1,3,2,4-diphosphadiboretane. This process is accompanied by a change of the *tert*-butyl groups from an *anti* orientation in **1** to a *syn* orientation in **5** as shown by X-ray crystallography.

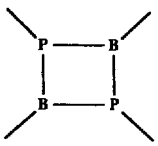
In contrast to the rapidly growing chemistry of 1,3,2,4-diphosphadiboretanes **B**[2], only two derivatives of the isomeric 1,2,3,4-diphosphadiboretanes **A** are known at present[3]. The former are thermodynamically more stable than the latter as exemplified by MO calculations of the two isomers of type $(HPBH)_2$ and $(HPBNH_2)_2$[4]. The higher thermodynamic stability of isomers of type **B** in comparison with **A** can be readily rationalized because the B–P bond energy exceeds that of the P–P and B–B bond energy. Consequently, in studying the chemistry of 1,2,3,4-diphosphadiboretanes there is the intrinsic possibility that derivatives of the 1,3,2,4-diphosphadiboretanes are formed. In this paper we report on the results of the reactions of some transition metal carbonyl complexes with compounds of type **A**.

Reactions

The model compound chosen for studies of the reactivity of type **A** diphosphadiboretanes was the four-membered 1,2,3,4-diphosphadiboretane **1**[3].



A



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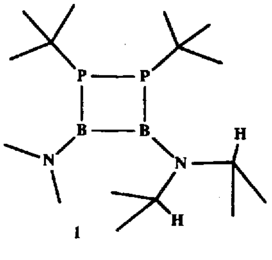

1

Treatment of **1** with $(CO)_5Cr \cdot THF$ in THF at ambient temperature results in a rather complex behavior. The ^{11}B-NMR spectrum of the solution shows signals at $\delta = 56, 46, 36$, and 30 in an intensity ratio of 2:4:2:1, and no pure product could be isolated from the mixture by fractional crystallization.

The 1:1 reaction beween **1** and $Fe_2(CO)_9$ seemed to be more straightforward. Only a single but rather broad signal at $\delta^{11}B = 49.5$ is observed in the ^{11}B-NMR spectrum of the resulting solution while three pairs of doublets are found in the ^{31}P-NMR spectrum at $\delta = 44.3/25.0$, 38.7/12.2 and 17.9/–2.3. The intensity ratio of these doublets is 0.6:1.3:1. These pairs of doublets can be assigned to the complexes **2**–**4**, each of them containing two chemically nonequivalent phosphorus atoms. The boron atoms are also chemically nonequivalent. However, no significant difference in the chemical shifts is to be expected for the ^{11}B-NMR signals because each boron atom is surrounded by a nitrogen, boron, and phosphorus atom[5], and the influence of the different ligands (Me_2N vs. $i\text{Pr}_2N$) should not greatly alter the shielding. In order to achieve an unambiguous assignment, at least one out of the three complexes should be independently synthesized, and its NMR data be determined. This was most readily performed for compound **4** by a combination of **1** and $Fe_2(CO)_9$ in a 1:2 ratio as shown in eq. (1). Compound **4** was isolated as a red solid, the ^{31}P-NMR spectrum of which displays doublets at $\delta = 44.3$ and 25.0 with $^1J(PP) = 106$ Hz.

On heating to 80 °C the bis(tetracarbonyliron) complex **4** decomposes with formation of **2** and **3** which are therefore thermally more stable than **4**. Irradiation of a solution of **4**

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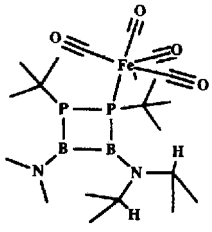

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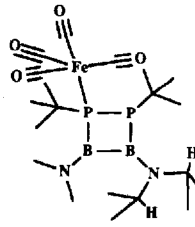

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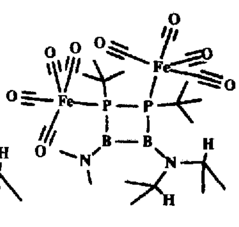
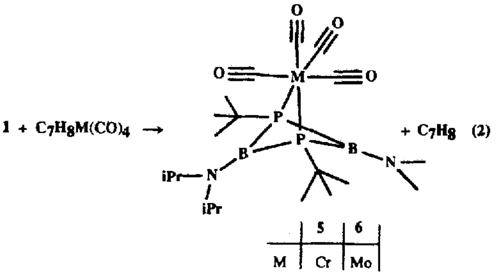


4

$$\mathbf{1} + 2\,Fe_2(CO)_9 \longrightarrow \mathbf{4} + 2\,Fe(CO)_5 \quad (1)$$



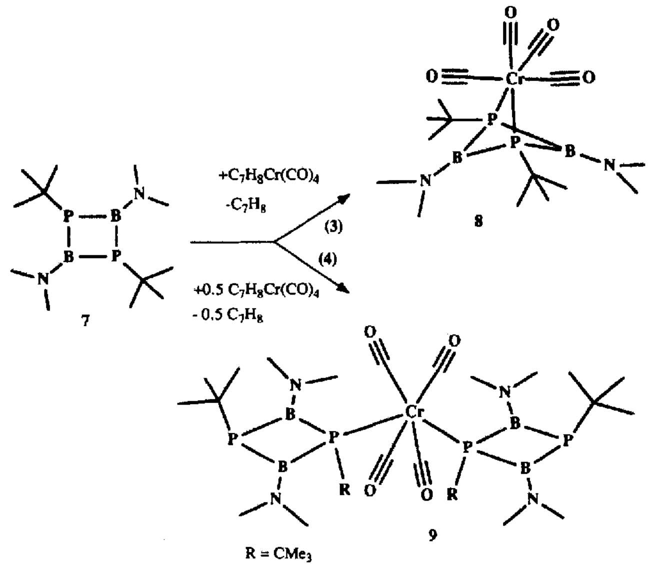
with the light of a mercury lamp results in the formation of **2** and **3** and decomposition into as yet unidentified products.

Treatment of **1** with tetracarbonyl(η^4-norbornadiene)-chromium or the corresponding molybdenum compound leads to displacement of norbornadiene by the BP ligand. However, the resulting tetracarbonylmetal complexes contain as a ligand a 1,3,2,4-diphosphadiboretane. Thus, isomerizations has occurred during the reaction as described by eq. (2).

Refluxing in hexane is required to achieve reaction (2) for compound **5** while the molybdenum complex **6** forms already at ambient temperature. The higher reactivity of $C_7H_8Mo(CO)_4$ compared with the chromium compound is well-known[6]. In several runs a weak ^{31}P-NMR signal at $\delta = -48$ is observed which points to the formation of a small amount of the ligand 1,3-di-*tert*-butyl-2-(diisopropylamino)-4-(dimethylamino)-1,3,2,4-diphosphadiboretane[2].

Since neither heating of **1** at 150°C in diglyme solution nor irradiation with a mercury lamp induces isomerization to the corresponding 1,3,2,4-diphosphadiboretane, the reaction described by eq. (2) does not proceed by isomerization of **1** prior to complex formation[7]. On the other hand, the tetracarbonyl complex **5** decomposes slowly at 80°C in toluene as shown by a signal at $\delta = -48$ in the ^{31}P-NMR spectrum which we assign to the free ligand.

For purposes of comparison, the reaction of $C_7H_8Cr(CO)_4$ with the 1,3,2,4-diphosphadiboretane **7**[8] was also investigated. In this case the norbornadiene ligand is already displaced at ambient temperature with the formation of complexes **8** and **9**. The latter compound is formed almost quantitatively in the presence of an excess of the ligand **7**. Eqs. (3) and (4) describe these reactions.



If more bulky amino groups are attached to the 1,3,2,4-diphosphadiboretane (e.g. two N*i*Pr$_2$ groups) no reaction with $C_7H_8Cr(CO)_4$ was observed by application of the same reaction conditions.

Spectroscopic Characterization of the Metal Carbonyl Complexes

The ^{1}H- and ^{13}C-chemical shifts observed for complexes **2**–**9** are listed in the experimental part, while ^{11}B- and ^{31}P-NMR data are summarized in Table 1.

Table 1. ^{11}B and ^{31}P chemical shifts of the 1,2,3,4-diphosphadiboretane **1** and its Fe(CO)$_4$ complexes **2**, **3**, and **4**, and the 1,3,2,4-diphosphadiboretane–carbonylmetal compounds **5**, **6**, **8**, and **9**

	1	2	3	4	5	6	7	8	9
$\delta^{11}B$	48.5	49.8	51.4	46.0	32.6	32.8	50.2	32.2	47.9
($h\frac{1}{2}$)	(367)	(502)	46.9	(450)	(264)	(454)		(369)	(560)
$\delta^{31}P$	−9.0	17.9	38.7	44.3	−57.3	−69.1	−46.8	−55.6	−19.2[a]
$^1J(PP)$		173	194	106					
$\delta^{31}P$	−26.6	−2.3	12.2	25.0					−40.3[a]
$^1J(PP)$		173	194	106					63

[a] d, N = 63 Hz.

The data in Table 1 clearly reveal the differences in shielding of the ^{11}B and ^{31}P nuclei for the metal complexes of the two isomeric diphosphadiboretanes: the boron nuclei of 1,2,3,4-diphosphadiboretanes are less shielded than those of the 1,3,2,4 isomers, **9** being an exception. This is due to the fact that compounds with a type **A** ligand can be considered as diborane(4) derivatives, and these boron nuclei are generally less shielded than those in derivatives of borane(3)[2,5,9] to which type **B** diphosphadiboretanes belong. Consequently, ^{11}B-NMR shifts for compounds **2**–**4** are diagnostic of derivatives of 1,2,3,4-diphosphadiboretanes. Although there are two chemically nonequivalent boron atoms present in compounds **2**–**4**, only the spectrum of **3** displays two separate signals. This is also the case for the free ligand **7**[2], the spectrum of which shows only a single signal. The better shielded boron atom in compound **3** was assigned to the Me_2NB group. It is expected to receive a higher electron density by π-bonding from the nitrogen atom because less steric hindrance is expected at this atom allowing a coplanar orientation with the ring plane.

It should be noted that the boron nuclei in the free 1,3,2,4-diphosphadiboretane ligands $(RPBNR'_2)_2$[2] give rise to resonances similar to those of their 1,2,3,4-isomers[3], and complexation of the former at both its phosphorus atoms results in a considerable high-field shift of the ^{11}B-NMR signal (≈18 ppm)[10]. This may be due to the fact that each boron atom now has two tetracoordinated P atom as neighbors, and the phosphonium-type character may inductively strengthen both BN σ and π bonding. In line with this argument is the increase in shielding of the boron nuclei in the tetracarbonylchromium complex **8**.

The observed deshielding of the ^{31}P nuclei on complexation of **1** with a $Fe(CO)_4$ fragment is in line with the ^{31}P-NMR data of $R_3PFe(CO)_4$ complexes[11,12]. Formation of the mononuclear complexes **2** and **3** causes a downfield shift for both ^{31}P nuclei, which is larger for the tetracoordinated P atom than for the tricoordinated P atom. Taking the average value for deshielding, we find an increasing effect relative to **1** in the order **2** ($\delta = 18.6$) < **3** ($\delta = 33.9$) < **4** ($\delta = 43.1$). Moreover, the $^{1}J(^{31}P^{31}P)$ coupling decreases in the order **3** > **2** > **4**. In the latter case there are no more phosphorus lone pairs, and there is probably less s character inherent in the P−P bond.

Inspection of the chemical shifts δ^{31}P for complexes **5** and **6** reveals an opposite trend as compared with compounds **2**−**4**. As can be seen there is a marked increase in the shielding of the ^{31}P nuclei relative to those in the ligand **7** and an even more drastic increase of the shielding compared with the ligand **1**. On the other hand, the P atom bound to the $Cr(CO)_4$ moiety in the $L_2Cr(CO)_4$ complex **9** becomes deshielded on complexation by 6.5 ppm. This indicates a different bonding situation for the $LM(CO)_4$ complexes **5**, **6**, and **8** and possibly reflects tetracoordination at P atoms with a rather flat pyramidal geometry[13].

According to the ^{1}H- and ^{13}C-NMR spectra of the carbonyliron complexes **2**−**4** we observe two signals each for the Me_2N group and six signals for the iPr$_2$N group indicating hindered rotation about the B−N bonds. Temperature-dependent spectra show coalescence of the resonances for the iPr$_2$N group of compound **2** at about 25 °C, and the barrier to rotation was determined as 62 kJ/mol. The same height of the rotation barrier was determined for the Me_2N group in compound **3**. No resonance coalescence for the Me_2N group in **2** and the iPr$_2$N group in **3** was observed up to 75 °C (where decomposition starts). Whether this observation is due to a stronger B−N bond as induced by the tetracoordinated P atom or to an increased steric hindrance remains an open question at this point. However, considering the results of the structure determination of compound **2** (v.i.), the former effect may dominate since the B−N bond length of the iPr$_2$N group becomes shorter by about 0.02 Å compared to that in the free ligand. This does not, however, exclude a steric effect.

Only single sets of signals are observed for the Me_2N group and the CH part of the NiPr$_2$ group in the ^{1}H- and ^{13}C-NMR spectra of **5** and **6**. There are, however, two signals in these spectra for the methyl groups of the isopropyl group. These coalesce at 326 K in **5** and at 330 K in **6**, leading to a rotational barrier about the B−N bond of 70.6 and 70.7 kJ/mol, respectively. These are typical values for BN bonds with considerable π bond character[14]. The signals of the protons of the *tert*-butyl group in compounds **5** and **6** appear as pseudo-triplets, due to coupling with the two nonequivalent ^{31}P nuclei. The structure suggested for compound **9** is in consonance with the ^{1}H- and ^{13}C-NMR data: there are two signals for the *tert*-butyl groups and two for the Me_2N group, indicating hindered rotation, and there is only a single signal for the carbonyl ^{13}C nuclei.

IR Spectra

Although the structures of the carbonylmetal complexes of the ligands **1** and **7** could be deduced from the NMR spectra, their IR spectra give additional information. Complexes **2**−**4** have $Fe(CO)_4$ groups in common. The NMR data suggest that the P atoms in each case are in an axial position of a trigonal bipyramid. If we assume local C_{3v} point group symmetry for the $LFe(CO)_4$ unit, then three IR bands associated with CO stretching vibrations should be expected for compounds **2**−**4** (**2**: 1924, 1954, 2035 cm^{-1}; **3**: 1925, 1953, 2034 cm^{-1}; **4**: 1937, 1961, 2033 cm^{-1}). There is no difference between the IR frequencies in the ν(CO) region for compounds **2** and **3**, while the IR bands of **4** are slightly shifted to higher wave numbers. This indicates a smaller degree of σ donor capacity of the P atoms in **4** as compared to **2** and **3**. On the other hand, the tetracarbonylmetal complexes **5**, **6**, and **8** should have local C_{2v} symmetry at the metal center. This requires three IR-active CO stretching vibrations, and these are observed (**5**: 1842, 1870, 1987 cm^{-1}; **6**: 1845, 1890, 2002 cm^{-1}; **8**: 1844, 1874, 1988 cm^{-1}). Finally, the IR spectrum of the tetracarbonylchromium complex **9** reveals only a single strong band in the CO stretching region at 1852 cm^{-1}, suggesting local D_{4h} symmetry for the $Cr(CO)_4L_2$ unit.

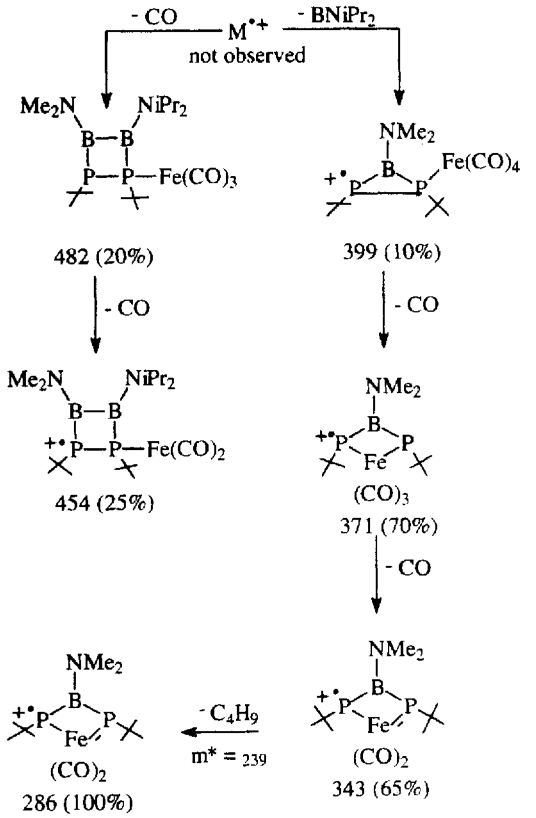
Mass Spectra

Complexes **2** and **3** behave rather similarly under electron impact conditions. Both lose the iPr$_2$NB fragment and two CO groups successively leading to a fragment of mass 286 as the peak of highest intensity. A second fragmentation path starts with loss of CO from the molecular ion which could not be observed. Scheme 1 shows the fragmentation and possible structures of the fragment ions for compound **2**.

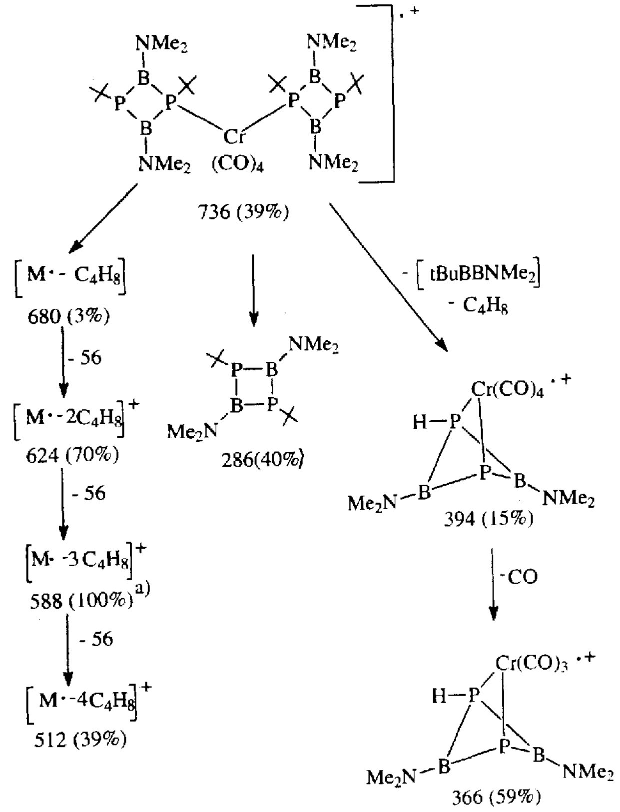
In contrast to **2** and **3**, the molecular ion of complex **5** loses only CO groups successively to form $[M - 4\ CO]^+$ (m/z = 394, 70%) before the heterocycle disintegrates. On the other hand, M^+ of complex $(CO)_4Cr(Me_2NBP\textit{t}Bu)_2$ (**8**) shows a fragmentation pattern characterized by loss of $Cr(CO)_4$ and by the peaks $[M^\cdot - C_4H_9]^+$ (m/z = 393, 70%) and $[M^\bullet - 3\ CO]^+$ (m/z = 366, 90%) with $M^{\bullet +}$ being of 100% relative intensity.

Finally, the decomposition of **9** in the mass spectrometer is summarized in Scheme 2. Its parent peak $M^{\bullet +}$ is ob-

Scheme 1. Fragmentation pattern of complex **2** in the mass spectrometer (70 eV). Only fragments with a relative intensity >10% are quoted



Scheme 2. Fragmentation pattern of the tetracarbonylchromium complex **8** in the mass spectrometer. Only fragments with a relative intensity >3% are shown



served with 30% relative abundance. Loss of C_4H_8 groups leads to a peak of mass 512 which we can consider a $Cr(CO)_4$ complex of two $(HPBNMe_2)_2$ ligands. It should be noted that no Me_3C radicals are formed which would have a $Cr(CO)_4$-bicyclobutane unit[16]. The parent ion disintegrates also in a different way by losing one of the two diphosphadiboretane ligands. The unobservable $(CO)_4CrL^{\bullet+}$ fragment seems to split off $H_2C{=}CMe_2$ and CO, leading to a fragment with a $Cr(CO)_3$ group. Additional fragments can be less definitely assigned.

Molecular Structures

Although the spectral data are in accord with the suggested structures the determination of structural details was considered important due to the unique character of some of these new compounds. Three of these were obtained as single crystals and were investigated by X-ray methods.

Compound **2** crystallizes from a hexane solution in the monoclinic system, space group $P2_1/c$. Figure 1 depicts the molecular structure in the solid state.

The B–B bond length [1.719(5) Å] is typical of a single bond[9,17], and the P–P bond in **2** is only slightly longer [2.237(1) Å] than the P–P single bond (2.21 Å)[18]. The two B–P bonds are on average (1.98 Å) on the longer side of B–P single bonds found in 1,3,2,4-diphosphadiboretanes[3,8,16]. This indicates no π bonding effects in the boron–phosphorus linkage, and this is further supported by the sum of the bond angles at P2 (295.1°) which, in principle, could participate in π overlap in contrast to the tetracoordinated P1. Neglecting the Fe–P bond, we obtain for the sum of bond angles at P1 290.8°. Expected for this atom is a somewhat longer B–P bond [1.989(4) Å] as a consequence of the higher coordination number.

Both B–N bonds of **2** are rather short (1.38 Å), indicating double bond characteristics. This is also supported by the interplanar angles $C_2N/B2B1P1$ of 11.7° (for B2) and 19.6° for $C_2N/B1B2P2$. The somewhat larger deviation from the ideal 0° interplanar angle is due to the bulkier $i$$Pr_2N$ group at B2 while the reduced steric demand of the Me_2N group leads to less twisting.

The iron atom resides in the center of a slightly distorted trigonal bipyramid with P1 and C4 in the axial positions. C4 is 1.760(5) Å apart from the Fe center. This is a shorter bond than to the equatorial Fe–C bonds [1.778–1.796(5) Å] and indicates that the P atom is a suitable σ donor in accord with a larger contribution of resonance form **E** to the ground state.

The four-membered P_2B_2 ring of **2** is not planar as indicated by a folding angle between the PB_2/B_2P planes of 160.3°. There is also a fairly large torsion angle N1–B1–B2–N2 of −57.6° in spite of the fact that the boron atoms are in an almost planar coordination environ-

Figure 1. ORTEP representation of the molecular structure of compound **2**. Thermal ellipsoids are represented on a 25% probability level. Selected bond lengths [Å] and angles [°]. Bond lengths: B1−B2 1.719(5), B1−P1 1.989(4), B2−P2 1.976(4), P1−P2 2.237(1), B1−N1 1.382(4), B2−N2 1.387(5), P2−C9 1.901(3), P1−C5 1.909(3), Fe1−P1 2.311(1), Fe1−C2 1.796(4), Fe1−C1 1.788(4), Fe1−C3 1.790(3), Fe1−C4 1.760(5). − Bond angles: B2−B1−P1 94.8(2), N1−B1−P1 122.8(3), N1−B1−B2 138.6(3), B1−B2−P2 97.2(3), N2−B2−P2 123.3(2), N2−B2−B1 138.0(3), B1−P1−P2 82.0(1), C9−P2−B2 101.5(2), C9−P2−P1 112.9(1), C5−P1−B1 108.5(2), B1−P1−Fe1 123.6(1), C5−P1−Fe1 115.1(1), B2−P2−P1 80.7(1), C5−P1−P2 100.3(1), C5−P1−B1 108.5(2), B2−B1−P1 94.8(2), N1−B1−P1 122.8(3), N1−B1−B2 138.6(3), P1−Fe1−C4 177.2(1), P1−Fe1−C3 90.2(2), P1−Fe1−C1 95.1(1), P1−Fe−C2 87.8(2)

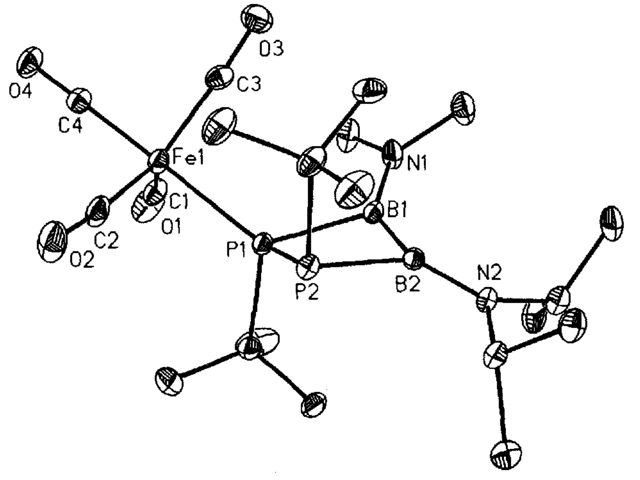
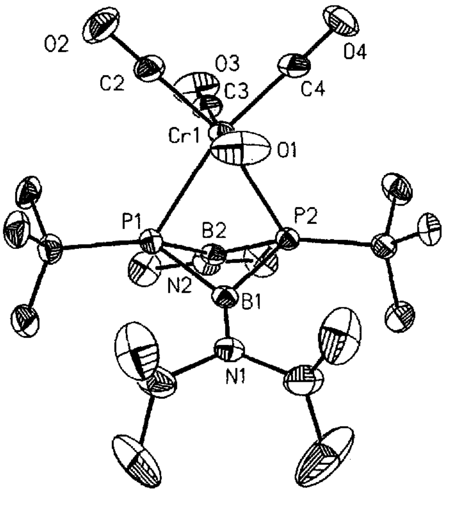
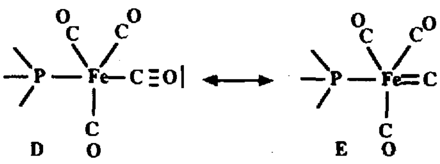


Figure 2. ORTEP representation of the molecular structure of complex **5** in the crystal. Thermal ellipsoids are drawn on a 25% probability level. Selected bond lengths [Å] and bond angles [°]: B1−P1 1.955(8), B1−P2 1.962(8), B2−P1 1.934(8), B2−P2 1.921(8), B1−N1 1.361(9), B2−N2 1.378(9), Cr1−P1 2.438(2), Cr1−P2 2.448(2), Cr1−C2 1.824(8), Cr1−C4 1.832(8), Cr1−C1 1.882(8), Cr1−C3 1.885(9). − Bond angles: P1−B1−P2 82.6(3), N1−B1−P1 137.1(6), N1−B1−P2 140.0(6), P2−B2−P1 84.2(3), N2−B2−P2 138.6(6), N2−B2−P1 136.7(6), B1−N1−C5 122.4(7), C5−N1−C8 117.9(7), B1−N1−C8 119.7(7), B2−N2−C19 124.3(7), B2−N2−C20 122.8(7), C19−N2−C20 112.8(6), P1−Cr1−P2 63.90(6), C2−Cr1−C4 95.1(3), C1−Cr1−C3 171.5(3)





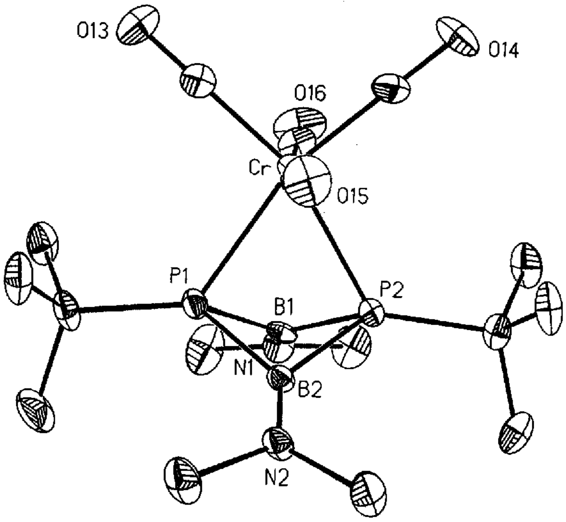
ment (356.2° for B1, 358.5° for B2). Similarly, the torsion angle B1−P1−P2−P2 is calculated as −15.2°. This leads to a P1 atom which resides 0.67 Å above the plane consisting of B1B2P2.

Figure 2 depicts the molecular structure of compound **5** which crystallizes as a toluene solvate. It can be noted that the ligand acts as a bidentate donor. However, the molecule can also be viewed at as a bicyclic system with a B_2P_2Cr skeleton. The four-membered B_2P_2 ring is strongly folded with an interplanar angle between the planes P1−B1−P2 and P1−B2−P2 of 123.7°. The boron and nitrogen atoms have a planar geometry with sums of bond angles varying from 359.6 to 360°. B−N bond lengths are short. Astonishingly, the B−N bond involving the diisopropylamino group [1.361(9) Å] seems to be shorter than that involving the dimethylamino group [1.378(9) Å]. However, taking the standard deviations into account, we can consider these two B−N bonds as not being significantly different. Nevertheless, the short distance provides evidence for B−N bonds with double bond character. In line with this conclusion is the fact that the C_2N planes are only slightly twisted out of the BP_2 plane (4.9° for $N1C_2$ and 8.1° for $N2C_2$). Moreover, the B−P bond lengths correspond to those found in 1,3,2,4-diphosphadiboretanes with tricoordinated B and P atoms[2]. Since the P atoms in **5** are tetracoordinated, the observed long B−P bonds are expected.

Another point of interest is the fact that the Cr−C bonds *trans* to a P atom are shorter than the Cr−C bonds in *cis* position. This is analogous to observations made for complex **2**. The geometry at Cr is distorted-octahedral due to the acute P−Cr−P bond angle [63.90(6)°] which leads to nonlinear P−Cr−C bond angles [164.5(2)° for C2−Cr1−P2 and 171.5(3)° for C3−Cr1−C1]. Moreover, the sums of the bond angles at P1 and P2 are 341.3 and 340.0°, respectively, neglecting the chromium atom. This rather flattened pyramidal phosphorus atom geometry is reminiscent of the almost planar geometry at the P atoms in $(mesPBNMe_2)_3Cr(CO)_3$[13].

The tetracarbonylchromium complex **8** is closely related to compound **5** and therefore suitable for gaining information on the steric effect of the diisopropylamino group on the structure. Figure 3 depicts its molecular structure. The B−P bond lengths and P−B−P as well as B−P−B bond angles demonstrate a rather symmetrically folded four-membered ligand system with an interplanar angle of P1B1P2/P1B2P2 = 124.2°. The two B−N bonds [1.36(1) and 1.35(1) Å] seem to be slightly different but by taking the standard deviations into account they can be considered to be of equal length. The nitrogen and boron atoms reside in a planar environment (sum of bond angles range from 359.4 to 359.9°), and the C_2N planes are twisted out of the respective BP_2 plane by 10.8° for $N1C_2$ and by 8.4° for $N2C_2$.

Figure 3. Molecular structure of compound **8** as ORTEP plot. Thermal ellipsoids are depicted with 25% probability. Selected bond lengths [A] and bond angles [°]: B1–P1 1.948(9), B1–P2 1.939(9), B2–P1 1.94(1), B2–P2 1.94(1), P1–Cr 2.431(2), P2–Cr 2.428(2), Cr–C16 1.90(1), Cr–C15 1.88(1), Cr–C13 1.843(8), Cr–C14 1.811(7), B1–N1 1.36(1), B2–N2 1.35(1). – Bond angles: N1–B1–P1 137.1(6), N1–B1–P2 139.0(6), P1–B1–P2 83.4(4), P1–B2–P2 83.7(5), N2–B2–P1 137.5(6), N2–B2–P2 138.1(6), P1–Cr–P2 64.34(6), C13–Cr–C14 98.1(3), P2–Cr–C13 161.8(2), P1–Cr–C14 164.3(2), C15–Cr–C16 171.9(4), B1–P1–C5 129.1(4), B2–P1–B1 82.3(4), Cr–P1–C5 128.0(3), B2–P1–Cr 87.3(2), B1–P1–Cr 85.6(2), C9–P2–B2 129.0(4), B1–P1–B2 82.7(4), C9–P2–Cr 127.9(2), B1–P2–Cr 85.9(2), B2–P2–Cr 87.5(2)



The coordination at the chromium atom shows a characteristic acute P1–Cr1–P2 bond angle of 64.35(6)° and bent P–Cr–C units [161.8(2) and 164.3(2)°]. As a consequence, the C13–Cr1–C14 bond angle is widened to 98.1(3)°.

Discussion

The 1,2,3,4-diphosphadiboretane **1** acts as a ligand forming tetracarbonyliron complexes. In contrast, complexation with $M(CO)_4$ fragments (M = Cr, Mo) results in the isomerization of a 1,2,3,4- to a 1,3,2,4-diphosphadiboretane. This isomerization is neither thermally nor photolytically induced because the free ligand is stable towards isomerization up to 150 °C and on UV photolysis. Since the formation of the tetracarbonyliron complexes proceeds *without* isomerization, the rearrangement observed with the tetracarbonylchromium and -molybdenum moiety suggests that steric effects or the "*cis*-bite" requirements of $M(CO)_4$ fragments may play a role. Ligand **1** is not suited for this kind of coordination because this requires the Me_3C groups bound to the P atoms to be in *cis* position. The rather high barrier to inverstion at P(III) is prohibitive, and the reaction is unlikely to proceed under the conditions employed for reactions (2).

The isomerization could be induced by the replacement of the olefin by formation of a metal-phosphorus bond. This would increase the steric strain in the ring molecule, and the adduct might disintegrate by cycloreversion into $[(CO)_4Cr]P(CMe_3){=}BNR_2$ and $Me_3C{-}P{=}BNR_2$ followed by cycloaddition and formation of the second P–Cr bond. This is, at the moment, a purely speculative suggestion but has an analogy in the formation of $[(CO)_5Cr]R'P{=}B{-}NR_2$ compounds from $(CO)_5Cr \cdot THF$ and $[R'P{=}BNR_2]_2$[8,19].

The molecular structure of the ring fragment in the $Fe(CO)_4$ complex **2** and most likely also of **3** and **4** is comparable with that of the free ligand **1**. There is no dramatic change as far as bond lengths and bond angles are concerned. The P–P and the B–B bonds are slightly elongated (both by about 0.02 Å). No change in the *trans* orientation of the *t*Bu group occurs on addition of the $Fe(CO)_4$ fragment. This is also true for the P–P–B ring angles while the ring angle at B1 becomes smaller by 2.5° and larger at B2 by 1.5°, resulting in an increase of the folding by 8°. As described for **2**, we find a P atom of the ligand in the axial position of the metal trigonal bipyramid. This is typical of $L{-}Fe(CO)_4$ complexes with a sterically demanding phosphane ligand[20]. Moreover, the axial Fe–C bond length is shorter than those of the equatorial CO groups. This shows that the 1,2,3,4-diphosphadiboretane ligand acts as a σ donor but not as a π acceptor ligand, and this effect results in a shortening of the $Fe{-}C_{ax}$ bond length by strengthening of the Fe–C π bonding due to the higher electron density at the iron center[12,20]. Moreover, we have to consider the ligand **1** as bulky, because the Fe–P bond in **2** [2.326(2) Å] is fairly long and corresponds closely to 2.364(1) Å found for $tBu_3PFe(CO)_4$ while it is only 2.237(2) Å for $Ph_2HPFe(CO)_4$[20].

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Experimental

All experiments were conducted under anhydrous and oxygen-free conditions by using Schlenk-type techniques and anhydrous solvents prepared by standard procedures and stored under N_2. – NMR: Bruker 200 WP, Jeol 270 and Jeol 400, $^{11}BF_3 \cdot OEt_2$ (external), 85% H_3PO_4 (external), C_6D_6 and TMS internal reference. Positive δ values refer to frequencies higher than the standards. – IR: Nicolet 520-FTIR. – MS: Varian CH7 (70 eV).

Octacarbonyl-μ-[1,2-di-tert-butyl-3-(diisopropylamino)-4-(dimethylamino)-1,2,3,4-diphosphadiboretane-P,P′]-diiron(0) (**4**): Compound **1** (0.38 g, 1.1 mmol)[3] and $Fe_2(CO)_9$ (0.80 g; 2.2 mmol) were dissolved in 20 ml of toluene, and the solution was stirred overnight. All volatile material was removed in vacuo. The remaining red solid was suspended in 10 ml of hexane. Insoluble products were removed by filtration. On cooling of the solution to 5 °C a red microcrystalline powder was obtained. Yield: 0.35 g of **4** (47%), m.p. 125–127 °C (dec.). – The residue which could not be dissolved in hexane was treated with tetrahydrofuran/hexane (1:1), but no solid product could be obtained from this mixture by cooling, although NMR-spectroscopic investigation showed that **4** was the main compound in this solution. – NMR (C_6D_6): $\delta^1H = 1.09$, 1.13, 1.25, 1.26 [d each, $^3J(HH) = 7$ Hz, 3 H, $CHCH_3$], 1.45, 1.49 [2 d, $^3J(PH) = 11$ Hz, 9 H, $C(CH_3)_3$], 2.57, 2.69 [both d, $J(PH) = 1$ Hz, 3 H, NCH_3], 3.80 [sept, $^3J(HH) = 7$ Hz, 1 H, $CHCH_3$], 3.97 [br. sept, $^3J(HH) = 7$ Hz, 1 H, $CHCH_3$]. – $\delta^{13}C = 26.9$, 23.8, 24.7, 26.1 (all s, $CHCH_3$), 32.7 [d, $^2J(PC) = 5$ Hz, $C(CH_3)_3$], 32.4 [d, $^2J(PC) = 3$ Hz, $C(CH_3)_3$], 39.8 [pseudo-t, $N = 9$ Hz, $C(CH_3)_3$], 40.4 [pseudo-t, $N = 14$ Hz, $C(CH_3)_3$], 45.0 [d, $^3J(PC) = 12$ Hz, NCH_3], 46.2 [d, ^{3}J(PC) = 9 Hz, $\mathrm{NCH_3}$], 55.6 [d, ^{3}J(PC) = 12 Hz, $\mathit{C}\mathrm{HCH_3}$], 58.1 [d, ^{3}J(PC) = 11 Hz, $\mathit{C}\mathrm{HCH_3}$], 216.5 [d, J(PC) = 9 Hz], 219.2 [d, J(PC) = 9 Hz]. – IR ($\mathrm{cm^{-1}}$, nujol/hostaflon/dichloromethane): $\tilde{\nu}$ = 3007 w, 2989 m, 2981 m, 2934 m, 2899 w, 2873 w, 2796 w, 2717 w, 2107 w, 2048 w, 2033 s (CO), 1961 s (CO), 1937 s (CO), 1539 w, 1522 m, 1483 w, 1471 w, 1455 m, 1409 m, 1396 m, 1369 m, 1353 w, 1329 w, 1313 w, 1184 m, 1166 m, 1147 m, 1122 w, 1047 w, 1020 w, 1012 w, 976 w, 936 w, 905 w, 867 w, 837 w, 819 w, 807 w, 733 w, 721 w, 673 w, 641 s, 625 s, 600 s, 560 w, 531 m, 483 w, 454 w, 433 w, 413 w, 388 w, 366 w, 349 w, 334 w. – MS: No spectrum could be obtained because **4** decomposed on heating to yield **2** and **3**. – $\mathrm{C_{24}H_{38}B_2Fe_2N_2O_8P_2}$ (677.8): calcd. C 42.53, H 5.65, N 4.13; found C 42.35, H 5.46, N 4.07.

Tetracarbonyl[1,2-di-tert-butyl-3-(diisopropylamino)-4-(dimethylamino)-1,2,3,4-diphosphadiboretane-P^1]iron(0) (**3**) *and Tetracarbonyl[1,2-di-tert-butyl-3-(diisopropylamino)-4-(dimethylamino)-1,2,3,4-diphosphadiboretane-P^2]iron(0)* (**2**): Compound **1** (0.30 g, 0.88 mmol) and $\mathrm{Fe_2(CO)_9}$ (0.32 g, 0.88 mmol) were dissolved in 10 ml of toluene. The resulting red solution was stirred overnight. All volatile components were then removed in vacuo. To the remaining red oil 10 ml of hexane was added. The suspension was warmed to 80 °C and immediately filtered. After cooling to ambient temp., the solution was stored at 5 °C. Microcrystalline **2** was then isolated by filtration. The remaining solution was stored at −18 °C, and **3** crystallized in red plates, which were isolated by filtration. After continuous cooling of the resulting solution a red precipitate was obtained, which was identified by its IR spectrum as 4. Yield: 0.030 g of **2** (7%), m.p. 140−145 °C (dec.) and 0.12 g of **3** (27%), m.p. 128−130 °C.

2: NMR ($\mathrm{C_6D_6}$): δ^{1}H = 1.09, 1.10, 1.16 [all as d, ^{3}J(HH) = 7.0 Hz, 3 H, $\mathrm{CHC}\mathit{H}_3$], 1.36 [d, ^{3}J(HH) = 6.5 Hz, 3 H, $\mathrm{CHC}\mathit{H}_3$], 1.34 [d, ^{3}J(PH) = 15 Hz, 9 H, $\mathrm{C(CH_3)_3}$], 1.49 [d, ^{3}J(PH) = 13 Hz, 9 H, $\mathrm{C(CH_3)_3}$], 2.63 (br. s, 6 H, $\mathrm{NCH_3}$), 3.74 [sept, ^{3}J(HH) = 6.5 Hz, 1 H, $\mathrm{C}\mathit{H}\mathrm{CH_3}$], 4.57 [sept, ^{3}J(HH) = 6.5 Hz, 1 H, $\mathrm{C}\mathit{H}\mathrm{CH_3}$]. – δ^{31}C = 24.5, 25.4, 25.9 (all $\mathrm{CH}\mathit{C}\mathrm{H_3}$), 30.6 [s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$], 33.1 [d, J(PC) = 12 Hz, $\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$], 36.0 [d, ^{1}J(PC) = 34 Hz, $\mathit{C}\mathrm{(CH_3)_3}$], 37.8 [d, ^{1}J(PC) = 19 Hz, $\mathit{C}\mathrm{(CH_3)_3}$], 45.0 (br., $\mathrm{NCH_3}$), 54.4 [d, ^{3}J(PC) = 11 Hz, $\mathit{C}\mathrm{HCH_3}$], 55.2 [d, ^{3}J(PC) = 15 Hz, $\mathit{C}\mathrm{HCH_3}$], 216.0 [d, ^{2}J(PC) = 14.2 Hz, CO]. – IR ($\mathrm{cm^{-1}}$, nujol/hostaflon/dichloromethane): $\tilde{\nu}$ = 2993 w, 2976 m, 2956 m, 2936 m, 2893 w, 2860 w, 2792 w, 2718 w, 2083 w, 2034 s (CO), 1953 s (CO), 1925 s (CO), 1533 w, 1513 m, 1473 m, 1453 m, 1442 m, 1406 m, 1389 w, 1368 m, 1351 w, 1325 w, 1318 w, 1183 m, 1164 m, 1143 m, 1129 m, 1118 m, 1112 w, 1067 w, 1047 w, 1014 w, 990 w, 978 w, 946 w, 929 w, 901 w, 868 w, 829 w, 811 w, 676 w, 623 s, 578 w, 531 m, 491 w, 474 w, 435 w, 417 w, 389 w, 358 w. – $\mathrm{C_{20}H_{38}B_2FeN_2O_4P_2}$ (509.9): calcd. C 47.11, H 7.51, N 5.49; found C 46.98, H 7.49, N 5.44.

3: NMR ($\mathrm{C_6D_6}$): δ^{1}H = 1.0 (br. m, 12 H, $\mathrm{CHC}\mathit{H}_3$), 1.29 [d, ^{3}J(PH) = 15 Hz, 9 H, $\mathrm{C(CH_3)_3}$], 1.48 [d, ^{3}J(PH) = 13 Hz, 9 H, $\mathrm{C(CH_3)_3}$], 2.57 (s, 3 H, $\mathrm{NCH_3}$), 3.05 (s, 3 H, $\mathrm{NCH_3}$), 3.25 (br., 1 H, $\mathrm{C}\mathit{H}\mathrm{CH_3}$), 4.25 (br., 1 H, $\mathrm{C}\mathit{H}\mathrm{CH_3}$). – δ^{13}C = 22.0, 23.0, 23.8, 25.4 (all s, $\mathrm{CH}\mathit{C}\mathrm{H_3}$), 31.5 [pseudo-t, N = 8 Hz, $\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$], 33.1 [dd, ^{3}J(PC) = 12, ^{2}J(PC) = 3 Hz, $\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$], 36.4 [dd, ^{1}J(PC) = 28, ^{2}J(PC) = 4 Hz, $\mathit{C}\mathrm{(CH_3)_3}$], 37.1 [dd, ^{1}J(PC) = 15, ^{2}J(PC) = 9 Hz, $\mathit{C}\mathrm{(CH_3)_3}$], 42.2 [d, ^{3}J(PC) = 12 Hz, $\mathrm{NCH_3}$], 44.7 [dd, ^{1}J(PC) = 15, ^{2}J(PC) = 9 Hz, $\mathit{C}\mathrm{(CH_3)_3}$], 42.2 [d, ^{3}J(PC) = 12 Hz, $\mathrm{NCH_3}$], 44.7 [d, ^{3}J(PC) = 14 Hz, $\mathrm{NCH_3}$], 49.8 (br., $\mathit{C}\mathrm{HCH_3}$), 55.0 (br., $\mathit{C}\mathrm{HCH_3}$), 216.0 [d, ^{2}J(PC) = 15.3 Hz, CO]. – IR ($\mathrm{cm^{-1}}$, nujol/hostaflon/dichloromethane): $\tilde{\nu}$ = 3963 w, 3940 w, 3880 w, 3824 w, 2971 s, 2940 s, 2924 s, 2898 s, 2861 s, 2792 w, 2713 w, 2444 w, 2355 w, 2086 w, 2035 s (CO), 1954 s (CO), 1924 s (CO), 1530 w, 1516 m, 1474 m, 1458 m, 1406 m, 1389 w, 1371 m, 1325 w, 1315 m, 1184 m, 1167 m, 1146 m, 1134 m, 1108 w, 1062 w, 1047 w, 1015 w, 991 w, 934 m, 895 w, 861 w, 837 w, 824 w, 808 w, 773 w, 757 w, 723 w, 681 w, 625 s, 577 w, 558 w, 538 m, 498 w, 476 w, 445 w, 421 w, 383 w, 362 w, 314 w. – MS, M/z (%): 482 (20) $\mathrm{[M - CO]^{\bullet +}}$, 454 (25) $\mathrm{[482 - CO]^{\bullet +}}$, 399 (10) $[\mathrm{M - B(N}\mathit{i}\mathrm{Pr_2)]^{\bullet +}}$, 371 (70) $\mathrm{[399 - CO]^{\bullet +}}$, 343 (65) $\mathrm{[371 - CO]^{\bullet +}}$, 286 (100) $[\mathrm{B(NMe_2)PP(}\mathit{t}\mathrm{Bu)Fe(CO)_2]^{+}}$. – $\mathrm{C_{20}H_{38}B_2FeN_2O_4P_2}$ (509.9): calcd. C 47.11, H 7.51, N 5.49; found C 47.21, H 7.50, N 5.52.

Tetracarbonyl[1,3-di-tert-butyl-2-(diisopropylamino)-4-(dimethylamino)-1,3,2,4-diphosphadiboretane-P,P′]molybdenum(0) (**6**): Compound **1** (0.14 g, 0.41 mmol) was added to tetracarbonyl(norbornadiene)molybdenum[21] (0.12 g, 0.41 mmol) (norbornadiene = bicyclo[2.2.1]hepta-2,5-diene). Addition of 12 ml of hexane gave an almost clear solution. After stirring for 12 h, a light yellow precipitate had formed which was isolated. This product consisted mainly of **6** and was slightly contaminated with **1** (^{31}P NMR). The solid was recrystallized from toluene to afford air-sensitive yellow crystals. Yield: 0.11 g of **6** (48%), m.p. 65 °C (dec.). – NMR ($\mathrm{C_6D_6}$): δ^{1}H = 1.02, 1.08 [both d, ^{3}J(HH) = 7 Hz, 6 H, $\mathrm{CHC}\mathit{H}_3$], 1.34 [pseudo-t, N = 18.6 Hz, 18 H, $\mathrm{C(CH_3)_3}$], 2.62 (s, 6 H, $\mathrm{NCH_3}$), 3.60 [sept, ^{3}J(HH) = 7 Hz, 2 H, $\mathrm{C}\mathit{H}\mathrm{(CH_3}$]. – δ^{13}C = 23.6, 24.1 (both $\mathrm{CH}\mathit{C}\mathrm{H_3}$), 31.6 [$\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$], 33.9 [pseudo-t, N = 22 Hz, $\mathit{C}\mathrm{(CH_3)_3}$], 45.0 (pseudo-t, N = 10.6 Hz, $\mathrm{NCH_3}$), 53.3 (br., $\mathit{C}\mathrm{HCH_3}$), 221.5 (CO). – IR ($\mathrm{cm^{-1}}$, nujol/hostaflon/dichloromethane): $\tilde{\nu}$ = 3858 w, 3700 w, 3668 w, 2968 m, 2970 m, 2962 m, 2792 w, 2062 w, 2012 w, 2002 s (CO), 1932 w, 1890 s (CO), 1845 s (CO), 1537 m, 1519 m, 1459 m, 1451 m, 1405 m, 1395 w, 1384 w, 1368 w, 1358 w, 1323 m, 1191 m, 1182 m, 1168 m, 1149 m, 1052 w, 1021 w, 1007 w, 977 w, 950 w, 934 w, 910 w, 869 w, 817 w, 787 w, 765 w, 751 w, 725 w, 694 w, 652 w, 620 s, 588 m, 546 w, 476 w, 449 w, 424 w, 410 w, 386 m, 351 w, 342 w. – $\mathrm{C_{20}H_{38}B_2MoN_2O_4P_2}$ (550.0): calcd. C 43.67, H 6.96, N 5.09; found C 43.77, H 7.14, N 5.14.

Tetracarbonyl[1,3-di-tert-butyl-2-(diisopropylamino)-4-(dimethylamino)-1,3,2,4-diphosphadiboretane-P,P′]chromium(0) (**5**): In a Schlenk flask equipped with a stirring bar a suspension of tetracarbonyl(norbornadiene)chromium (0.090 g, 0.35 mmol) in 5 ml of hexane was combined with a solution of **1** (0.12 g, 0.35 mmol) in 5 ml of hexane. The addition of approximately 10 ml of hexane led to a clear solution. The mixture was then kept at reflux by heating in an oil bath (105 °C) for 2 h. On cooling a yellow solid formed which was isolated by filtration. This solid was dried briefly in vacuo, and its purity was ascertained by NMR and elemental analysis. Recrystallization from 10 ml of toluene gave single crystals of **5**, which contained approximately 1 molecule of toluene per formula unit. Yield: 0.08 g of **5** (45%), m.p. 155−157 °C (dec.). – NMR ($\mathrm{C_6D_6}$): δ^{1}H = 1.03, 1.09 [2 d, ^{3}J(HH) = 6.8 Hz, 6 H, $\mathrm{CHC}\mathit{H}_3$], 1.36 [pseudo-t, N = 18.5 Hz, 18 H, $\mathrm{C(CH_3)_3}$], 2.53 [s, 6 H, $\mathrm{N(CH_3)_2}$], 3.50 [sept, ^{3}J(HH) = 6.8 Hz, 2 H, $\mathrm{C}\mathit{H}\mathrm{CH_3}$]. – δ^{13}C = 23.5, 24.1 (both $\mathrm{CH}\mathit{C}\mathrm{H_3}$), 31.4 [$\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$], 34.4 [pseudo-t, N = 13.3 Hz, $\mathit{C}\mathrm{(CH_3)_3}$], 44.9 (pseudo-t, N = 12 Hz, $\mathrm{NCH_3}$), 53.9 (br., $\mathit{C}\mathrm{HCH_3}$), 220.6, 233.2 (both CO). – IR ($\mathrm{cm^{-1}}$, nujol/hostaflon/dichloromethane): $\tilde{\nu}$ = 2976 m, 2931 m, 2897 w, 2869 m, 2052 w, 1987 s (CO), 1927 w, 1870 s (CO), 1842 s (CO), 1536 w, 1520 m, 1495 w, 1461 m, 1452 m, 1408 m, 1395 w, 1369 m, 1324 m, 1188 m, 1165 m, 1146 m, 1124 w, 1083 w, 1052 w, 1020 w, 1005 w, 997 w, 942 w, 906 w, 882 w, 815 w, 806 w, 759 w, 730 m, 684 s, 648 s, 640 s, 579 w, 548 w, 503 w, 479 m, 442 w, 409 w, 343 w. – MS, m/z (%): 506 (20) $\mathrm{[M]^{\bullet +}}$, 478 (10) $\mathrm{[M - CO]^{\bullet +}}$, 450 (20) $\mathrm{[M - 2\,CO]^{\bullet +}}$, 422 (80) $\mathrm{[M - 3\,CO]^{\bullet +}}$, 394 (70) $\mathrm{[M - 4\,CO]^{\bullet +}}$. – $\mathrm{C_{20}H_{38}B_2CrN_2O_4P_2}$ (506.1): calcd. C 47.47, H 7.57, N 5.54; found C 46.31, H 7.58, N 5.68. – After crystallisation from toluene, **5**. $\mathrm{C_6H_5CH_3}$ was obtained; calcd. C 53.28, H 7.91, N 4.78; found C 52.5, H 7.75, N 4.76. On complete removal of the toluene in vacuo a partial decomposition was observed.

Tetracarbonyl[1,3-di-tert-butyl-2,4-bis(dimethylamino)-1,3,2,4-diphosphadiboretane-P,P′]chromium(0) (**8**): 1,3-Di-*tert*-butyl-2,4-bis(dimethylamino)-1,3,2,4-diphosphadiboretane[22] (0.35 g, 1.2 mmol) and tetracarbonyl(norbornadiene)chromium (0.31 g, 1.2 mmol) were dissolved in 30 ml of hexane. The clear yellow solution was stirred overnight after which time a fine, yellow powder had formed. After stirring for another day the solid was isolated by filtration. The solution contained **9** (preparation see below) in low concentration (NMR). The solid also contained **8** and **9** but in a 1:1 ratio. After addition of 5 ml of toluene to the solid, filtration and cooling of the resulting solution at −20 °C, **8** separated as yellow single crystals. Yield: 0.07 g of **8** (12%), m.p. 180 °C (dec. starts at 60 °C). – NMR (C_6D_6): δ^1H = 1.27 [pseudo-t, *N* = 18.6 Hz, 18 H, $C(CH_3)_3$], 2.50 (6 H, NCH_3). – $\delta^{13}C$ = 31.3 [$C(CH_3)_3$], 32.9 [pseudo-t, *N* = 25.9 Hz, $C(CH_3)_3$], 44.5 (pseudo-t, *N* = 12.2 Hz, NCH_3), 220.6 (pseudo-t, *N* = 13.7 Hz, CO), 233.3 (pseudo-t, *N* = 15.2 Hz, CO). – IR (cm^{-1}, nujol/hostaflon/dichloromethane): $\tilde{\nu}$ = 3963 w, 3837 w, 3815 w, 3747 w, 3689 w, 3663 w, 3024 w, 2982 m, 2962 m, 2940 s, 2924 s, 2893 m, 2869 m, 2793 m, 2350 w, 2087 w, 2052 w, 2014 w, 2005 w, 1988 s (CO), 1874 s (CO), 1844 s (CO), 1548 m, 1529 s, 1472 m, 1461 s, 1408 s, 1363 m, 1346 m, 1334 m, 1283 w, 1190 s, 1173 s, 1144 s, 1101 w, 1083 w, 1072 w, 1052 s, 1017 m, 993 w, 952 w, 936 w, 905 m, 882 m, 818 m, 792 w, 770 w, 720 w, 685 s, 650 s, 578 w, 550 m, 480 s, 445 w, 439 w, 419 w, 410 w, 378 w, 351 w, 331 w. – MS, *m/z* (%): 450 (100) $[M]^{\bullet+}$, 393 (70) $[M - tBu]^+$, 365 and 366 (90) $[M - tBu - CO]^+$ and $[M - 3\,CO]^{\bullet+}$, 337 and 338 (80) $[M - tBu - 2\,CO]^+$ and $[M - 4\,CO]^{\bullet+}$, 286 (80) $[M - Cr(CO)_4]^{\bullet+}$. – $C_{16}H_{30}B_2CrN_2O_4P_2$ (450.0): calcd. C 42.71, H 6.72, N 6.23; found C 41.07, H 6.41, N 6.21.

Tetracarbonylbis[trans-1,3-di-tert-butyl-2,4-bis(dimethylamino)-1,3,2,4-diphosphadiboretane-P]chromium(0) (**9**): 1,3-Di-*tert*-butyl-2,4-bis(dimethylamino)-1,3,2,4-diphosphadiboretane (**7**) (0.32 g, 1.12 mmol) was dissolved in 5 ml of hexane. 50% of a solution of tetracarbonyl(norbornadiene)chromium (0.14 g, 0.56 mmol) in 7 ml of hexane was added from a dropping funnel. The mixture was stirred for 24 h. Then the rest of the metal carbonyl solution was added, and the mixture was stirred for 4 d. The yellow precipitate which had formed was isolated by filtration and recrystallized from 5 ml of toluene. Yield 0.15 g of **9** (35%), m.p. 190 °C (dec.). – NMR (C_6D_6): δ^1H = 1.48, 1.50 [both d, $^3J(PH)$ = 12.7 Hz, 18 H, $C(CH_3)_3$], 2.90 (s, 12 H, NCH_3), 3.16 [d, $^4J(PH)$ = 1.1 Hz, 12 H, NCH_3]. – $\delta^{13}C$ = 32.7 [d, $^3J(PC)$ = 3.8 Hz, $C(CH_3)_3$], 35.0 [d, $^3J(PC)$ = 7.6 Hz, $C(CH_3)_3$], 34.3 [d, $^1J(PC)$ = 4.7 Hz, $C(CH_3)_3$], 37.9 [dd, $^1J(PC)$ = 8.0, $^3J(PC)$ = 3.8 Hz, $C(CH_3)_3$], 45.2 (pseudo-t, *N* = 16.1 Hz, NCH_3), 44.6 (pseudo-t, *N* = 14.2 Hz, NCH_3), 227.6 [t, $^2J(PC)$ = 7.6 Hz, CO]. – IR (cm^{-1}, nujol/hostaflon/dichloromethane): $\tilde{\nu}$ = 3019 w, 2968 m, 2955 m, 2926 s, 2883 m, 2857 m, 2787 w, 2710 w, 2003 w, 1915 w, 1852 s (CO), 1822 w, 1711 w, 1505 s, 1474 m, 1459 m, 1406 m, 1394 s, 1362, 1277 w, 1262 w,

Table 2. Relevant crystallographic data pertaining to data collection and structure solution

Compound	2	5	8
Chem. formula	$C_{20}\,H_{38}\,B_2\,Fe\,N_2\,O_4\,P_2$	$C_{27}\,H_{46}\,B_2\,Cr\,N_2\,O_4\,P_2$	$C_{16}\,H_{30}\,B_2\,Cr\,N_2\,O_4\,P_2$
Form wght.	509.93	598.22	449.98
Cryst size [mm]	0.3x0.4x0,8	0.2x0.3xo.45	0.3x0.3x0.4
Cryst system	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/c	P2(1)/n	P2(1)/n
a, [Å]	9.699(2)	10.220(2)	10.642(4)
b, [Å]	28.278(6)	19.321(4)	14.588(2)
c, [Å]	10.366(2)	17.133(4)	15.795(3)
α, [°]	90.00	90.00	90.00
β, [°]	107.74(3)	92.67(1	94.94(3)
γ, [°]	90.00	90.00	90.00
V, [Å^3]	2707.9(10)	3379.4(12)	2443.0(11)
Z	4	4	4
ρ(calc), [Mg/m^3]	1.251	1.176	1.223
μ [mm^{-1}]	0.701	0.464	0.620
F(000)	1080	1272	944
Index range	$0 \le h \le 11$ $-32 \le k \le 32$ $-11 \le l \le 0$	$-1 \le h \le 10$ $0 \le k \le 20$ $-18 \le l \le 18$	$-1 \le h \le 6$ $0 \le k \le 16$ $-18 \le l \le 18$
2 θ [°]	48.22	45.00	47.98
Temp, [K]	293(2)	233	293(2)
Refl. collected	5583	5234	3215
Refl. unique	2825	4395	2522
Refl. observed (4σ)	2226	2919	1943
R (int.)	0.0417	0.0459	0.0315
No. variables	292	320	254
Weighting scheme[1] x/y	0.0440/0.7119	0.1253/3.5378	0.0170/7.5237
GOOF	1.009	1.080	1.270
Final R (4σ)	0.0339	0.0714	0.0567
Final wR2	0.0802	0.1946	0.1169
Larg. res. peak [e/Å^3]	0.341	0.974	0.342

[1] $w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2F_c^2)/3$

1192 m, 1185 m, 1176 m, 1127 s, 1052 m, 1019 m, 989 w, 935 w, 905 w, 892 w, 843 w, 828 w, 811 m, 766 m, 751 m, 727 w, 671 s, 637 s, 572 w, 507 w, 481 m, 430 w, 408 w, 390 w, 375 w, 351 w, 316 w. – MS, *m/z* (%): 736 (30) $[M]^{\bullet+}$, 680 (5) $[M - 56]^{\bullet+}$, 624 (70) $[M - 2 \times 56]^{\bullet+}$, 568 (100) $[624 - C_4H_8]^{\bullet+}$, 512 (30) $[568 - C_4H_8]^{\bullet+}$. – $C_{28}H_{60}B_4CrN_4O_4P_4$ (735.9): calcd. C 45.69, H 8.22, N 7.61; found C 45.93, H 8.24, N 7.58.

X-Ray Structure Determinations: Single crystals of compounds **2**, **5**, and **8** were mounted in glass capillaries under argon. X-ray data were collected with Mo-K_α radiation with a Siemens P4 or a Nicolet R3 diffractometer. Computer programs were XS[23a] and SHELXL 93[23b]. The structures were solved by direct methods. The refinement proceeded with anisotropic description of nonhydrogen atoms and isotropic thermal parameters for hydrogen atoms as riding model. No absorption correction was applied. Relevant data are compiled in Table 2. While refinement could be performed smoothly for compounds **2** and **8**, restraints had to be imposed on compound **5** which contained 0.75 molecules of toluene of per molecule **8**. The toluene molecules are disordered. The phenyl group of toluene was included in the refinement as an idealized C_6 unit. Details on the crystal structure determination are available at the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, and may be ordered by quoting the depository number CSD-405305 (**5**), 405306 (**2**), 405307 (**8**), the names of the authors and the literature citation.

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