1,3,5-Triphenyl-2,4,6-trimesityl-1,3,5,2,4,6-triphosphatriborinane: A 6π-Electron Heteroaromatic Ligand☆

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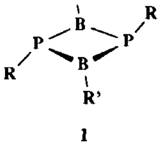
The preparation of tricarbonyl(η^6-1,3,5-triphenyl-2,4,6-trimesityl-1,3,5,2,4,6-triphosphatriborinane)chromium (**4**) is reported. Its X-ray structure reveals an orientation of the $Cr(CO)_3$ moiety with respect to the almost planar B_3P_3 ring typical of an arene metal tricarbonyl complex.

We have recently demonstrated that the four-membered tetraorganyl-1,3,2,4-diphosphadiboretanes **1** react with metal carbonyls $M(CO)_n$ with formation of complexes of type **1** · $M(CO)_{n-2}$[1]. These can be regarded either as compounds containing an η^4-bonded ligand or as *nido* clusters. The results suggest that other BP heterocycles, particularly the six-membered 1,3,5,2,4,6-triphosphatriborinanes (1,3,5-triphospha-2,4,6-triboracyclohexanes), may serve as strong and vesatile η^6 ligands because their planar ring system is regarded as heteroaromatic[2]. In this context we have been able to synthesize the tricarbonylchromium complex **2**[1] and more recently the complex **4** from $Cr(CO)_3(CH_3CN)_3$ and 2,4,6-trimesityl-1,3,5-triphenyltriphosphatriborinane (**3**) according to eq. (1). Compound **4** is a red, almost air-stable compound which dissolves readily in many organic solvents.



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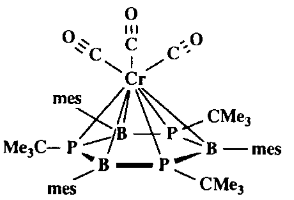

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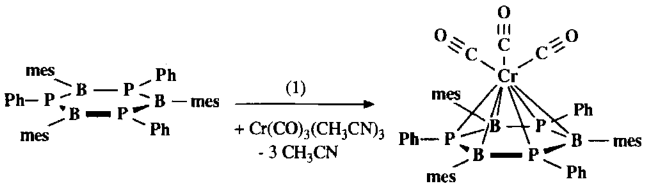

3 **4**

The ^{11}B- and ^{31}P-NMR spectra exhibit only one signal demonstrating that these ring atoms remain chemically equivalent. Their chemical shifts indicate that both the B and P atoms are more shielded in **4** as compared with the free ligand **3**, the shift differences being 59.7 and 25.5 ppm, respectively. Two ^1H and two ^{13}C resonances are observed for the methyl groups in 2,6-positions of the mesityl groups, indicating that there is no free rotation around the BC bonds. Moreover, the methyl group inequivalence requires that the *B*-mesityl and the *P*-phenyl groups are oriented more or less perpendicular to the ring plane. For steric reasons, the substituents cannot be coplanar. Although NMR data are in accord with an η^6-ligand geometry, no further information on details of the structure of **4** can be deduced. Therefore, the structure of **4** was determined by X-ray methods[2].

Figure 1 depicts the molecular structure of **4** in the solid state. The boron–chromium bond distances fall in two categories: two are short and one is longer. This also holds, although less pronounced, for the phosphorus–chromium bond lengths. The Cr–B distances are only slightly longer than the Cr–P distances with the exception of the bond Cr–B1. The B_3P_3 ring is almost planar with a largest deviation of 0.088 Å for atom P3 from the mean plane. This results primarily from imperfectly planarized P atoms, particularly at atom P3. This is also indicated by the sum of the bond angles of the P atoms that deviate slightly from the ideal 360° (sum of bond angles B–P–B', B–P–C, and B'–P–C is 357(+/−1)°), while the sum of analogous bond angles at the boron atoms is 360°. A slight puckering of the six-membered ring is therefore noted with the largest dihedral angles at P2–B2–P3–B3 (14.9°) and B2–P2–B1–P1 (−14.9°). Although this may suggest a

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strong deviation from planarity, the plane through the three P atoms and the three B atoms intersect with an angle of only 2.6°.

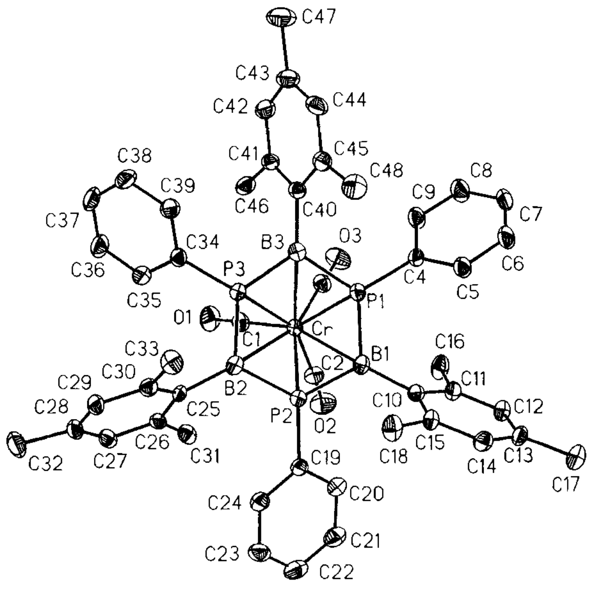

Figure 1. ORTEP-type representation of the molecular structure of **4**. Thermal ellipsoids represent a 25% probability. Hydrogen atoms are omitted. Selected bond distances [Å]: Cr−P1 2.506(3), Cr−P2 2.516(3), Cr−P3 2.525(3), Cr−B1 2.558(7), Cr−B2 2.512(6), Cr−B3 2.525(7), Cr−C1 1.814(7), Cr−C2 1.819(7), Cr−C3 1.839(6), C−O 1.156−1.175(8), P1−B1 1.840(7), P1−B3 1.865(7), P2−B2 1.833(7), P2−B1 1.844(6), P3−B2 1.865(7), P3−B3 1.842(6), P1−C4 1.798(5), P2−C19 1.801(6), P3−C34 1.801(6), B1−C10 1.586(9), B2−C25 1.584(8), B3−C40 1.575(8). − Selected bond angles [in °]: P1−Cr−P2 76.5(1), P1−Cr−P3 75.3(19), P2−Cr−P3 76.2(1), P1−Cr−B1 42.6(2), P1−Cr−B2 93.9(2), P2−Cr−B1 42.6(1), P3−Cr−B1 92.1(2), P3−Cr−B2 43.5(2), P3−Cr−B3 42.8(1), B1−Cr−B2 79.8(2), B1−Cr−B3 81.1(2), B2−Cr−B3 82.0(2), B1−P1−B2 124.4(3), B1−P2−B3 126.2(3), B2−P3−B3 126.0(3), P1−B1−P2 115.2(3), P2−B2−P3 114.5(3), P1−B3−P3 112.0(3), B1−P1−C4 117.0(3), B3−P1−C4 115.5(3), P1−B1−C10 120.1(4), P2−B1−C10 123.8(4)

On average, complexation of **3** by the $Cr(CO)_3$ fragment has no significant effect on the BP bond lengths (1.843 Å in **3**[2], 1.845 Å in **4**). However, the lengths of the BP bonds in **4** differ up to 0.032 Å in contrast to **3** with 0.006 Å. Also, the bond angles in **4** are similar to those in **3**, e.g. they are larger on the P atoms (average 125.5°, 124.5° in **2**) than on the B atoms (average 113.9°, 114.9° in **2**).

The normals of the mes groups to the normal of the mean B_3P_3 plane form angles ranging from 59.5 to 70° and, similarly, for the phenyl groups from 34.1 to 40°, and all of them are twisted toward the best B_3P_3 plane in the same sense as is already the case with the parent molecule **3**[2]. This feature is also evident from Figure 1 which also demonstrates that the vectors of the CO groups almost point midway to the B−P bonds on the opposite side which is typical of arene π complexes. It should be noted, however, that the methyl groups C16, C31, and C46 are placed between the CO groups and would prevent an eclipsed conformation for steric reasons. This becomes more apparent from the space-filling model in Figure 2, with C1−H31B, C2-H9A, and C3-H16B contacts falling within the range expected for van der Waals contacts (2.492−2.721 Å).

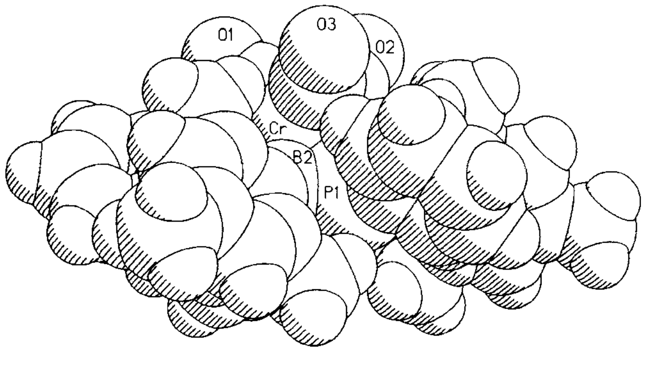

Figure 2. Space-filling model of **4** with a side-on view to show the staggered conformation of methyl groups and the CO ligands

Compound **4** shows longer Cr−P bonds as compared with carbonyl(σ-phosphane)chromium complexes, e.g. *fac*-$Cr(CO)_3(PH_3)_3$ [2.346(4) Å][3], $(Ph_3P)Cr(CO)_5$ [2.422(1) Å][4], *fac*-$Cr(CO)_3(PEt_3)_3$ [2.429(8) Å][5], or even for the π complex (π-2,4,6-$Ph_3C_6H_2P$) · $Cr(CO)_3$ [2.480(4) Å][6]. However, the Cr−P bond length in the related $(mesB{=}PCMe_3)_2Cr(CO)_4$ is as short as 2.400(3) Å[1]. This result is certainly due to the different geometry.

Although there is some asymmetry of the complex in the solid state, NMR data are in accord with a more symmetrical structure (C_{3v}). Information that can be deduced from the data at hand suggests that the ligand **3** behaves as a 6π-electron donor towards the $Cr(CO)_3$ fragment.

The geometry of **4** resembles more closely that of tricarbonyl(hexamethylbenzene)chromium[7] with the staggered conformation of the $Cr(CO)_3$ moiety rather than that of the borazine complex $[EtB{=}NEt]_3Cr(CO)_3$[8], where the CO bond vectors point in the direction of the nitrogen atoms. Moreover, the planar borazine ring becomes noticeably more puckered on addition of the $Cr(CO)_3$ fragment than the B_3P_3 unit in the case of **4**. This result lends further credit to the "aromatic" character of **3** and other planar derivatives of the triphosphatriborinane ring[2]. However, at the present time it cannot be decided whether the specific conformation of **4** is due only to steric effects of the bulky substituents or additionally electronically determined. Inspite of this still open question it can be concluded that the ligand **3** is a more efficient electron donor than either hexamethylbenzene[9] or the hexaalkylborazines[10] as demonstrated by its CO stretching frequencies [1945, 1884 cm^{-1} for **4**, 1962, 1888 cm^{-1} for $(MeC{=}CMe)_3Cr(CO)_3$), and 1963, 1867 cm^{-1} for $(MeN{=}BMe)_3Cr(CO)_3$], and this holds also for **2** [ν(CO) = 1930.7, 1863.0 cm^{-1}[1]]. In addition, it is noteworthy that the structure of **4** places this molecule in the series of *nido*-metallaboranes[11] as is the case with the recently described diphosphadiboretane metal carbonyls[1]. Consequently, one can envision that other BP heterocyclic ligands will behave in a fashion similar to their isoelectronic carbocycles, and this point is under active investigation in our laboratories.

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Experimental

Tricarbonyl(1,3,5-triphenyl-2,4,6-trimesityl-1,3,5,2,4,6-triphosphatriborinane)chromium (**4**): 1.04 g (4.01 mmol) of solid $(CH_3CN)_3Cr(CO)_3$ was added to 0.68 g (0.95 mmol) of $(mesBPPh)_3$ (**3**) dissolved in 60 ml of dioxane. After stirring for 3 h, 30 ml of dioxane was removed in vacuo and 40 ml of fresh dioxane was added. After stirring overnight the color of the reaction mixture had changed from orange to dark red. After removal of small amounts of insoluble material by filtration, the solvent was removed from the filtrate in vacuo, the residue treated with 40 ml of toluene, and an insoluble residue was separated again by filtration. The red product which remained after all the solvent had been evaporated in vacuo was recrystallized from a mixture of 20 ml of THF and 5 ml of hexane at −18°C. Yield: 0.70 g of **4** (0.82 mmol, 87%); m.p. >250°C (dec.). – ^{1}H NMR (400 MHz, C_6D_6): δ = 2.09 (s, 9H, *p*-CH_3), 2.57 (s, 9H, *o*-CH_3), 2.61 (s, 9H, *o*-CH'_3), 6.67 (m, $9H_{mes+ph}$), 6.72 [d, $^5J_{(P,H)}$ = 7.3 Hz, 3H, *p*-H_{ph}], 6.79 (s, 3H, *m*-H'_{mes}), 7.33 (s, 6H, *m*-H_{ph}). – ^{13}C NMR (50 MHz, C_6D_6): δ = 21.1 (s, *p*-CH_3), 23.8 (s, *o*-CH_3), 26.8 (s, *o*-CH'_3), 127.9 (*ipso*-C_{ph}), 128.6 (s, *m*-C_{mes}), 129.1 (s, *m*-C'_{mes}), 130.4 (s, *o*-C_{ph}), 130.7 (s, *m*-C_{ph}), 134.9 (s, *p*-C_{ph}), 138.2 (s, *p*-C_{mes}), 141.0 (s, *o*-C_{mes}), 142.6 (s, *o*-C'_{mes}), 236.7 (s, CO). – ^{31}P NMR (81 MHz, C_6D_6): δ = −17.2, *h*(1/2) = 150 Hz. – ^{11}B NMR (64 MHz, C_6D_6): δ = 27.2, *h*(1/2) = 710 Hz. – IR (CH_2Cl_2, cm^{-1}): $\nu(C{\equiv}O)$ = 1945.2, 1884.2. – $C_{48}H_{48}B_3CrO_3P_3$ (850.3): calcd. C 67.81, H 5.69; found C 64.07, H 5.77.

X-Ray Structure Analysis of **4**: Nicolet R3m four-circle diffractometer, Mo-K_α radiation, graphite monochromator, single crystal (dimension 0.25 × 0.3 × 0.4 mm) sealed in a glass capillary. – *Crystal Data:* $C_{48}H_{48}B_3CrO_3P_3$, formula weight 850.2, monoclinic, a = 12.306(7), b = 18.290(16), c = 20.464(10) Å, β = 102.95(4)°, V = 4489(5) Å^3, space group = $P2_1/n$, d = 1.258 Mg/m^3, Z = 4, μ = 3.91 cm^{-1}, $F(000)$ = 1776. – *Data Collection:* 2Θ range 3–48° in $+/-h$, k, l, scan range = 0.9°, scan speed = 1.7–29.3°/min, 2 check reflections monitored after every 48 intensity measurements, 7576 collected data, 7092 independent reflections (R_{int} = 2.62%), 4470 reflections considered observed [$2.7\sigma(I)$]. – *Solution and Refinement:* SHELXTL PLUS system (VMS), structure solved with direct methods, full-matrix least-squares refinement, nonhydrogen atoms refined anisotropically, H atoms: riding model, fixed isotropic U, data:parameter ratio = 8.5:1, R = 6.79%, R_w = 5.82%, GOOF = 1.33, largest difference peak = 0.40 eÅ^{-3} [12].

☆ Dedicated to Professor Dr. Dr. h. c. mult. *E. O. Fischer* on the occasion of his 75th birthday.

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