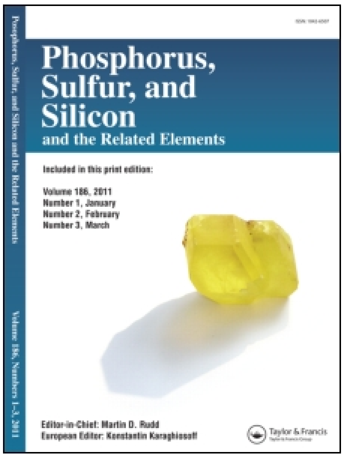

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COORDINATION CHEMISTRY OF THE CAGE $P_2(BNPr^i_2)_3$

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Abstract The coordination properties of the cage compound $P_2(BNPr_2)_3$ toward $Fe_2(CO)_9$, $Cr(CO)_5NMe_3$ and $W(CO)_5NMe_3$ were studied, and the molecular structure of $(CO)_4FeP_2(BNPr_2)_3$ was determined by single crystal X-ray diffraction methods.

INTRODUCTION

In recent years, there has been a great deal of attention given to the systematic development of transition metal cluster compounds and, to a lesser degree, main group element clusters. In the latter case, most of the developments have occurred with polyphosphines and PN, PO and PS cages. Our groups have turned attention to the possibility of constructing cage compounds rich in boron and phosphorus atoms, and we have previously reported on the formation of a novel trigonal bipyramidal cage, $P_2(BNPr^i_2)_3$. The molecular structure determination of the cage showed that the two phosphorus atoms occupy the two axial sites with the trigonal plane composed of three $BNPr^i_2$ groups. The internal B-P-B angle was found to be quite acute, 68.9(2)°. Given this structure, it was of interest to determine if the phosphorus atoms would display Lewis basicity toward transition metal fragments. We report here on the reaction of the cage with $Fe_2(CO)_9$, $Cr(CO)_5NMe_3$ and $W(CO)_5NMe_3$.

RESULTS

The Group VI metal carbonyl amine complexes were combined in equimolar amounts with $P_2(BNPr^i_2)_3$ in hexane and stirred for 48 hours. The solvent was then removed by vacuum evaporation and the resulting yellow oils were pumped on at 45°C for two days to remove any residual metal carbonyl, $M(CO)_6$. Subsequent purifications resulted in yellow oils: Yield $Cr(CO)_5[P_2(BNPr^i_2)_3]$ (**1**) 85%. Anal. Calc for $C_{23}H_{42}N_3O_5B_3P_2Cr$: C, 47.07; H, 7.16; N, 7.16. Found: C, 47.47; H, 7.35; N, 7.02. Yield $W(CO)_5[P_2(BNPr^i_2)_3]$ (**2**) 48%. Both compounds displayed a parent ion in the mass spectra: **1** m/e 587; **2** m/e 718, along with anticipated fragment ions. The infrared spectra of the oils in cyclohexane showed three bands in the carbonyl region as expected for $M(CO)_5L$ complexes: **1** 2053, 1956 and 1933 cm^{-1} and **2** 2064, 1954 and 1931 cm^{-1}. These may be compared with the related bands in the amine complexes $Cr(CO)_5NMe_3$ (hexane)^2 2070, 1933 and 1915 cm^{-1} and $W(CO)_5NMe_3$ (cyclohexane)^3 2073 and 1944. The small shifts to lower frequency for the high frequency a_1 mode in **1** and **2** suggests that $P_2(BNPr^i_2)_3$ may be only a slightly better σ donor than NMe_3 toward the $M(CO)_5$ fragments.

The ^{31}P NMR spectra for **1** and **2** are informative with respect to the coordination chemistry. The ligand displays a single resonance at δ -13.0 while solutions of the complexes in C_6D_6 show two inequivalent phosphorus environments: **1** δ -45.8(d), -61.0(d) J_{PP} = 49.0 Hz; **2** δ -82.9(br), -67.2(d) J_{PP} = 54.1 Hz. Similar AB patterns have been noted for $P(OCH_2)_3P$ and its metal carbonyl complexes.^{4} The resonances at δ -45.8 in **1** and δ -82.9 in **2** are much broader than the doublets in **1** at δ -61.0 and in **2** at δ -67.2, and the broader resonances are assigned to the metal coordinated phosphorus site. The $^{11}B\{^1H\}$ NMR spectra for **1** and **2** show single resonances at δ 36.0 and δ 34.4 (rel $BF_3{\bullet}OEt_2$), respectively. These are shifted only slightly from the value for the free ligand, δ 40.5. The inequivalent phosphorus atoms also impose inequivalency in the isopropyl groups as indicated by the $^{13}C\{^1H\}$ and ^1H NMR spectra which are listed here: **1**, $^{13}C\{H\}$ δ 56.8 (d of d, J_{CP} = 10.6 Hz, $J_{CP'}$ = 3.7 Hz, $\underline{C}H(CH_3)_2$), 46.4 (d, J_{CP} = 3.9 Hz, $\underline{C}H(CH_3)_2$), 25.5 (d, J_{CP} = 8.7 Hz $\underline{C}H_3$) 21.9 (s, $\underline{C}H_3$), ^1H δ 4.9 (mult; $C\underline{H}(CH_3)_2$), 3.3 (mult, $C\underline{H}(CH_3)_2$) 1.4 (d, J_{HH} = 6.8 Hz $C\underline{H}_3$) 1.1 (d, J_{HH} = 6.7 Hz $C\underline{H}_3$); **2**, $^{13}C\{^1H\}$ δ 56.5 (d of d, J_{CP} = 11.9 Hz, $J_{CP'}$ = 3.6 Hz, $\underline{C}H(CH_3)_2$), 46.6 (d, J_{CP} = 4.4 Hz, $\underline{C}H(CH_3)_2$), 25.5 (d, J_{CP} = 8.3 Hz $\underline{C}H_3$), 21.8 (s, $\underline{C}H_3$), ^1H δ 4.8 (mult, $C\underline{H}(CH_3)_2$), 3.2 (mult, $C\underline{H}(CH_3)_2$), 1.3 (d,J_{HH} = 6.8 Hz, $C\underline{H}_3$, 1.1 (d, J_{HH} = 6.7 Hz, $C\underline{H}_3$). Although inequivalence is evident, an assignment of the stereochemical arrangement of the specific Pr^i groups, with respect to the metal substituted phosphorus atom, has not been made.

The equimolar reaction of the Group VIII metal carbonyl $Fe_2(CO)_9$ with $P_2(BNPr^i_2)_3$ in hexane was also examined. After stirring for one day, the resulting red solution was filtered, the filtrate evaporated to dryness and pumped on to remove $Fe(CO)_5$. The residue was recrystallized from cold hexane. Yield $Fe(CO)_4[P_2(BNPr^i_2)_3]$ (**3**) 65%. The mass spectrum of **3** showed a parent ion $\underline{m}/\underline{e}$ = 563 and several anticipated fragment ions: $\underline{m}/\underline{e}$ = 506 ($Fe(CO)_2[P_2(BNPr^i_2)_3]$; 470 $Fe(CO)[P_2(BNPr^i_2)_3]$; 451 $Fe[P_2(BNPr^i_2)_3]$. The infrared spectrum (hexane) showed three carbonyl bands, 2038, 1965 and 1931 cm^{-1}, as expected for an axially substituted $Fe(CO)_4L$ complex. These data compare favorably with infrared data for $Fe(CO)_4[P(NMe_2)_3]$[5] and a series of complexes $Fe(CO)_4[P(Cl)(NR_2)_2]$[6]. The ^{31}P NMR spectrum is similar to that described above for the $M(CO)_5L$ complexes: δ -59.8 (broad, coupling unresolved), -99.0 (d, J_{PP} = 39 Hz). It is interesting to note that both resonances are shifted upfield of those found in the $Cr(CO)_5L$ complex. The $^{11}B\{^1H\}$ NMR spectrum contains a single signal at δ 32.5. The $^{13}C\{^1H\}$ and ^1H NMR spectra also show inequivalent Pr^i groups: 3, $^{13}C\{^1H\}$ δ 55.2 (d, J_{CP} = 8.5 Hz $\underline{C}H(CH_3)_2$), 46.2 (d, J_{CP} = 5.6 Hz, $\underline{C}H(CH_3)_2$), 25.6 (d, J_{CP} = 8.1 Hz $\underline{C}H_3$), 22.1(s $\underline{C}H_3$); ^1H δ 5.0 (broad $C\underline{H}(CH_3)_2$), 3.1 (broad $C\underline{H}(CH_3)_2$), 1.2 (d, J_{HH} = 7.5 Hz, $C\underline{H}_3$) 1.1 (d, J_{HH} = 7.5 Hz, $C\underline{H}_3$).

The molecular structure of 3 was unambiguously confirmed by single crystal X-ray diffraction techniques, and a view of the molecule is shown in Figure 1. The molecule displays a mirror plane which contains the Fe-C(1)-O(1) vector and the P(1)-P(2)-B(1)-N(1)-C(5) plane. The $Fe(CO)_4$ fragment has an approximate trigonal bipyramidal geometry with $P_2(BNPr^i_2)_3$ occupying an axial site. The carbonyl ligands in the $Fe(CO)_4$ trigonal plane are slightly distorted toward the coordinated axial phosphorus atom as indicated by the average in-plane angle Fe-C-O (178.2)°. The average equatorial Fe-CO bond distance is 1.765(15)Å, and the axial Fe-C(2)O distance is 1.749(13)Å. These distances are comparable with the ranges of distances found in $Ph_3PFe(CO)_4$ 1.792(2)-1.796(4)Å[7] and $(Me_2N)_3PFe(CO)_4$[5] 1.781(5)-1.793(6)Å. The Fe-P(1) bond distance, 2.260(3)Å, is longer than those found in $Ph_3PFe(CO)_4$, 2.244(1)Å, and in $(Me_2N)_3PFe(CO)_4$, 2.245(1)Å. Either steric effects or poor σ donor/π acceptor properties would justify the longer distance found in 3. Within the accuracy of the structure determination, the structural parameters of the ligand fragment are little changed by complexation. For example, P(1)-B(1)

1.972(11)Å, P(1)-B(2) 1.938(11)Å, P(2)-B(1) 1.949(17)Å and P(2)-B(2) 1.955(9)Å compare with 1.969(8)Å in the ligand. The B(1)-N(1) and B(2)-N(2) distances 1.349(19)Å and 1.376(11)Å are similar to B-N, 1.339(16)Å in the free ligand. The internal ligand cage angles

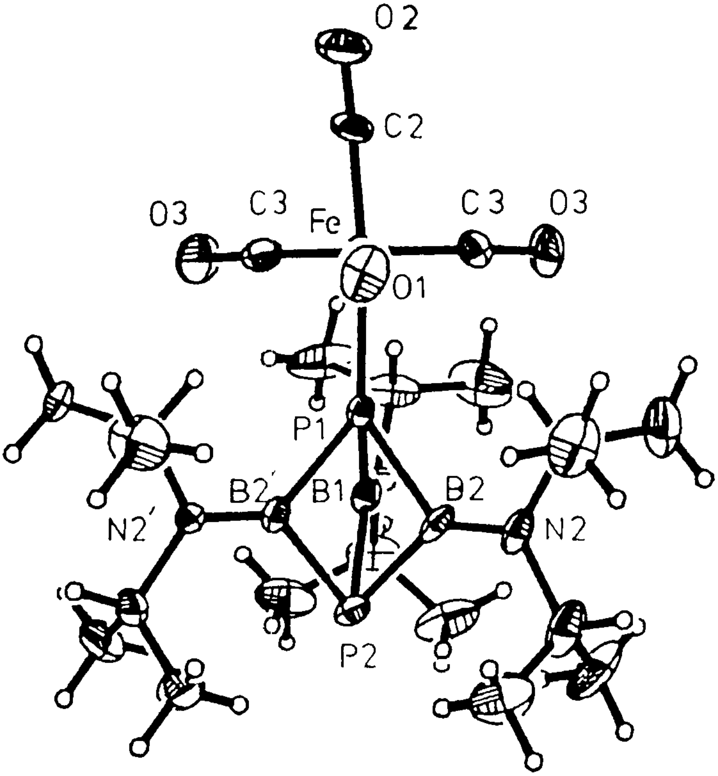

Figure 1. View of the structure of $Fe(CO)_4[P_2(BNPr^i_2)_3]$. Orthorhombic, space group Cmca (no. 64), a = 15.949(5)Å, b = 15.473(4)Å, c = 27.207(9)Å, Z = 8, $\rho_{calcd} = 1.24$ g cm^{-3}. $R_F = 9.1\%$, $R_{wF} = 8.1\%$ on 1637 unique data with $F \geq 3.5\sigma(F)$.

B(1)-P(1)-B(2) 71.9(5)°, B(2)-P(1)-B(2') 75.3(5)°, B(1)-P(2)-B(2') 72.1(4)° and B(2)-P(2)-B(2') 74.5° are slightly larger than that in the free ligand, 68.9(2)°. This trend would be expected in response to metal-phosphorus binding. Similarly, the internal angles about boron close down slightly as indicated by P(1)-B(1)-P(2) 92.7(6)° and P(1)-B(2)-P(2) 93.5(4)° compared to the free ligand, 98.5(5)°.

Several attempts were made to coordinate both phosphorus sites with metal carbonyl fragments; however, even in the presence of large excesses of metal carbonyl, no evidence for bimetallic coordination was found. Further studies of this and related PB clusters are in progress, and it appears that several new families of cage ligands may evolve.

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