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Molecular Structure and Dynamics of $TaCl(\eta^4\text{-}C_{10}H_8)[(CH_3)_2PC_2H_4P(CH_3)_2]_2$

Sir:

Among the higher coordination numbers, seven-coordinate species represent a commonly found, but poorly understood class. Theoretical studies imply that the three frequently found geometries[1,2]—D_{5h}, pentagonal bipyramid; C_{2v}, monocapped trigonal prism; C_{3v}, monocapped octahedron—are energetically close; facile interconversions are expected. Although dynamic NMR behavior has been observed in seven-coordination,[3] no definitive observation of the intimate mechanism for isomerization between idealized geometries has appeared. We report herein the preparation of $TaCl(\eta^4\text{-}C_{10}H_8)(dmpe)_2$ (**1**) (dmpe = 1,2-(bisdimethylphosphino)ethane), its structure, and direct observation of the pentagonal bipyramid to monocapped trigonal prism interconversion.

Dropwise addition of 3.5 equiv of sodium naphthalene to a benzene solution of $(dmpe)_2TaCl_4$[4] which contained excess naphthalene gave a deep red solution. Removal of solvent and naphthalene in vacuo, chromatography (silica gel, THF eluent), and crystallization of the residue from toluene-hexane afforded **1** in poor yield. Treatment of a THF solution of **1** with an additional 2 equiv of sodium naphthalene and subsequent addition of HSO_3F or $MeOSO_2F$ gave $TaH(\eta^4\text{-}C_{10}H_8)(dmpe)_2$ (**2**) and $TaMe(\eta^4\text{-}C_{10}H_8)(dmpe)_2$ (**3**), respectively.[5]

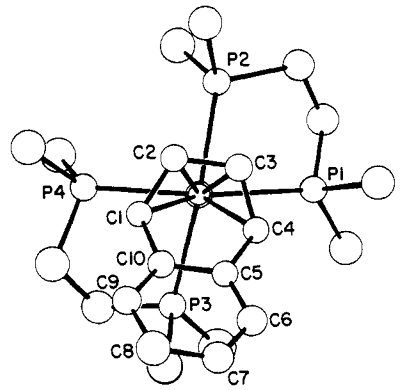


Figure 1. The molecular structure of $TaCl(\eta^4\text{-}C_{10}H_8)(dmpe)_2$ viewed along the Ta-Cl vector. Rotation of naphthalene by 45° about this vector yields the monocapped trigonal prismatic structure found for $TaCl(CO)_2(dmpe)_2$.[4] Ta-C distances (Å): Ta-C(1), 2.403 (9); Ta-C(2), 2.255 (9); Ta-C(3), 2.250 (9); Ta-C(4), 2.383 (9).

Crystals of $TaCl(\eta^4\text{-}C_{10}H_8)[(CH_3)_2PC_2H_4(CH_3)_2]_2$ are red monoclinic prisms: space group $P2_1/C$; a = 10.343 (3), b = 10.281 (3), c = 24.642 (7) Å; β = 97.39 (1)°; Z = 4. The 4019 independent reflections for which $I/\sigma(I) > 1.96$ were measured on a Syntex $P2_1$ diffractometer (crystal-monochromated Mo Kα radiation). Full-matrix, least-squares refinement of positional and isotropic thermal parameters for all nonhydrogen atoms has converged to a conventional R factor[6] of 0.048.

The molecular structure of the complex (Figure 1) may be considered to be an approximate pentagonal bipyramid (cf. monocapped octahedral $TaH(CO)_2(dmpe)_2$[3h] and monocapped trigonal prismatic $TaCl(CO)_2(dmpe)_2$[4]) with the midpoints of the C(1)-C(2) and C(3)-C(4) bonds, Ta, P(1), P(4), and Cl forming the pentagonal plane (all with deviations < 0.24 Å), and P(2) and P(3) the apices of the bipyramid, the P(2)-Ta-P(3) angle being 154.0 (1)°. These distortions from the idealized pentagonal bipyramidal geometry are presumably a reflection of the bidentate nature of the ligands. In this complex, the diphosphine ligands are undisordered,[7] a probable consequence of steric interactions between the diphosphines and the naphthalene moiety. The angle between the η^4-diene residue of naphthalene (carbon atoms C(1) through C(4)) and the uncoordinated portion is 43.3°, which lies within the range reported (37.4-47.9°) for the few structurally characterized η^4-arene complexes.[8]

The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **1** at −36 °C (Figure 2) is consistent with the ABCD pattern anticipated from the structural data. Coalescence to an A_4 system (55 °C) implies a process equilibrating P(1)-P(4). Similar behavior is observed for **2** and **3**.

At 70 °C the $^1H\text{-}\{^{31}P\}$ NMR spectrum shows an AA′BB′ pattern (δ 5.6, 4 H) assigned to H(6)-H(10) and a complex multiplet at δ 2.9 (H(2), H(3)),[9] consistent with the presence of an effective mirror plane in the naphthalene residue. The resonances attributable to H(1), H(4) are obscured by the dmpe methylene signals.[10] The observation of distinct resonances for bound and unbound naphthalene rings in the high-temperature limit rules out mechanisms involving transfer of the $TaClP_4$ group between ring systems. Further, at 70 °C the dmpe methyl groups occur as two distinct sets (δ 0.2, 12 H, and δ 0.5, 12 H): those directed toward Cl and those directed toward the diene fragment. This eliminates "arm-off, arm-on" processes and any mechanism involving migration of Cl or naphthalene about the P(1), P(2), P(3), P(4) plane.

On cooling to −50 °C the dmpe methyl and H(6)-H(9) resonances become more complex. The H(2), H(3) signal is

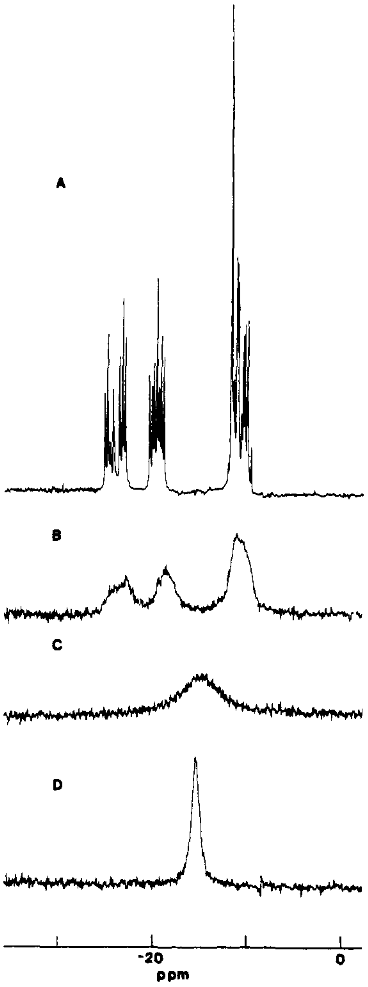
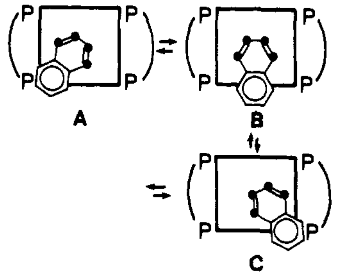


Figure 2. The ^{31}P-{^{1}H} NMR spectra of TaCl(η^4-C$_{10}$H$_8$)(dmpe)$_2$ in toluene-d_8: (a) −36 °C, (b) −15 °C, (c) 35 °C, and (d) 55 °C.

resolved into two multiplets (δ 3.4, 1 H, and δ 2.5, 1 H) in agreement with the lack of symmetry found for the ground state (Figure 1). Identical spectral details are observed for **2** and **3**.

These data are consistent only with rotation of naphthalene about the Ta–Cl axis, a mechanism which necessarily traverses the monocapped trigonal prismatic intermediate B.[11,12]



These observations constitute detection of the pentagonal bipyramid to monocapped trigonal prism interconversion via rotation of a pair of adjacent ligands about the common C_2 axis of the idealized geometries. That is, one of the equatorial and the two axial ligands in the pentagonal bipyramidal arrangement become the unique ligand and two of the four symmetry related vertices in the monocapped trigonal prismatic structure, respectively. By comparison of the discoincidence indices[13] for all plausible C_{2v} to D_{5h} paths, we have shown this mechanism to be that of least motion[14] for interconversion of the idealized geometries. Moreover, electronic barriers associated with this process are estimated to be small on the basis of symmetry arguments.[15] This mechanism is analogous to that suggested by Muetterties[16] and by Hoffmann et al.[2e]

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(12) Intermediate B can be equally well represented by an ortho-quinoidal resonance form. This possibility is mitigated by observation of identical spectral behavior for TaCl(1,3-cyclohexadiene)(dmpe)$_2$ (4). 4 was prepared in poor yield by prolonged reduction of TaCl$_2$(dmpe)$_2$^{4} with sodium amalgam in the presence of excess cyclohexadiene and isolated by fractional crystallization. An analytically pure sample could not be obtained, but the proper ^{1}H and ^{31}P NMR and high-resolution mass spectral data were obtained.

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Thiapen Chemistry. 1.
Synthesis of 1,3,4,6-Tetrathiapentalene-2,5-bis(dialkyliminium) Salts

Sir:

We describe here the ready synthesis of anion salts of the novel 1,3,4,6-tetrathiapentalene-2,5-bis(dialkyliminium) ring system (**1**, abbreviated thiapendiiminium).[1] Previously, 2-dialkyliminium salts of 1,3-dithiole system (e.g., **2**) have been