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Seven-Coordinate Complexes of Tantalum(I)

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Reduction of $TaCl_5$–dmpe (dmpe = 1,2-bis(dimethylphosphino)ethane) mixtures affords $(dmpe)_2TaCl_4$; further reduction yields $(dmpe)_2TaCl_2$. Reductive carbonylation of $(dmpe)_2TaCl_2$ gives $(dmpe)_2Ta(CO)_2Cl$, which can be further reduced to the unisolated $Na[(dmpe)_2Ta(CO)_2]$. This anion is converted to $(dmpe)_2Ta(CO)_2X$ (X = Cl, Br, CH_3, and CN) on treatment with HCl, HBr, CH_3I, and HCN, respectively. The reactions with anhydrous acids have been shown to proceed through $(dmpe)_2Ta(CO)_2H$ by infrared monitoring experiments. On the basis of ^{31}P and ^{1}H NMR and infrared data, the seven-coordinate derivatives, $(dmpe)_2Ta(CO)_2X$, are proposed to have a capped trigonal prismatic structure. Similar criteria support a cis structure for the anion, $Na[(dmpe)_2Ta(CO)_2]$.

Introduction

In comparison to four-,[1] five-,[1,2] and six-coordination,[1,3] the stereochemistry of seven-coordinate complexes is poorly understood.[1,4] Empirical correlations or a priori arguments generally do not permit a confident assessment of either overall geometry or site preferences within a given ligand arrangement. These features arise because of the small energy differences between different isomers whether considered from a molecular orbital point of view[4g] or steric framework.[4b–e] Furthermore, since the barriers associated with isomer interconversion are small, inequivalent, chelating, or bridging ligand systems induce sufficient distortion that the relation of a real structure to a reference geometry is frequently not obvious.[1,4f] Consequently, a large body of structural information does not provide definitive stereochemical guidelines.[4a,f]

In part, the structural data suffers from a sparsity of information regarding systematically varied compounds. Ideally, a series of complexes in which one ligand is variable would reveal site preferences and trends in overall geometry within the restrictions imposed by the other ligands. With strong field ligands, the choice of such a system is largely restricted to d^4 metal ions. A further limitation is purely tactical: there must be sufficient spectroscopic handles to allow an unambiguous structural assignment. In this paper we report the preparation and stereochemistry of $Ta(dmpe)_2(CO)_2X$ (dmpe = 1,2-bis(dimethylphosphino)ethane) derivatives designed toward these ends.[5]

Experimental Section

Solvents were purified by distillation from sodium benzophenone ketyl. Tantalum pentachloride[7] and 1,2-bis(dimethylphosphino)ethane[8] were prepared by literature methods. Sodium naphthalene was prepared by direct reaction and titrated immediately before use.[9]

Manipulations throughout were performed in vacuo or under an atmosphere of prepurified nitrogen. Infrared, 100-MHz ^{1}H and 40.5-MHz ^{31}P NMR, 9.5-GHz ESR, and mass spectra were obtained on Perkin-Elmer 457A, Varian XL-100, Varian E-109, and AEI MS-9 spectrometers, respectively. ^{31}P NMR chemical shifts are relative to external 85% phosphoric acid. Elemental analyses were by Galbraith Laboratories Inc., Knoxville, Tenn.

$(dmpe)_2TaCl_4$ (1). To 2.01 g (5.63 mmol) of $TaCl_5$ dissolved in 100 ml of benzene containing 15% THF was added 1.69 g (11.3 mmol) of dmpe and 5 ml of 0.5% Na(Hg). The initial yellow suspension gave a deep blue solution after shaking for 5 min. The supernatant was decanted and the residue was washed with 3 × 20 ml of benzene. The combined extracts were filtered through a Celite pad and evaporated to dryness. The resulting gummy solid was recrystallized from hot benzene–heptane, affording 1.96 g (3.15 mmol, 56%) of **1** as blue crystals.

Anal. Calcd for $C_{12}H_{32}Cl_4P_4Ta$: C, 23.12; H, 5.18; Cl, 22.76. Found: C, 22.62; H, 4.97; Cl, 23.85.

The mass spectrum exhibited an isotope envelope centered at *m/e* 629, whose pattern agrees nearly exactly with that calculated for the parent ion (M^+). Additional features were centered at *m/e* 479 $(M - dmpe)^+$, 329 $(M - 2dmpe)^+$. Peaks corresponding to successive chloride loss were also present.

$(dmpe)_2TaCl_2$ (2). To 10.0 g of **1** (16.1 mmol) dissolved in 150 ml of THF was added 400 g of 0.75% Na(Hg) and the mixture was stirred vigorously. After 2 h the solution was deep brown. The supernatant was decanted and the residue was washed with 3 × 50 ml of THF. The combined extracts were filtered through a Celite pad and evaporated to dryness. Recrystallization of the residue by slow cooling of a saturated hexane solution to −78 °C with rigorous exclusion of air gave 7.32 g (13.26 mmol, 83%) of **2** as red-brown crystals: mass spectrum *m/e* 551 $[^{12}C_{12}{}^{1}H_{32}{}^{35}Cl_2{}^{31}P_4Ta]^+$, 516 $[P - Cl]^+$.

Anal. Calcd for $C_{12}H_{32}Cl_2P_4Ta$: C, 26.10; H, 5.84. Found: C, 25.59; H, 5.80.

The ESR spectrum of **2** in benzene exhibited an eight-line pattern, $g = 1.943$; ^{31}P hyperfine was not resolved.

Reaction of 1 with Methyllithium. To 483 mg of **1** suspended in 30 ml of ether containing 1 ml of dioxane was added 5.5 equiv of MeLi. After 30 min of stirring, **1** had completely dissolved giving an orange solution. Evaporation of the solvent and slow cooling of a hexane extract (5 ml) gave red-brown crystals. Mass spectra exhibited features at *m/e* 643 $[^{12}C_{12}{}^{1}H_{32}{}^{81}Br_2{}^{31}P_4{}^{181}Ta]^+$, 597 $[^{12}C_{12}{}^{1}H_{32}{}^{81}Br^{35}Cl^{31}P_4{}^{181}Ta]^+$, and 551 $[^{12}C_{12}{}^{1}H_{32}{}^{35}Cl_2{}^{31}P_4{}^{181}Ta]^+$. In each case the correct isotope envelope was observed.

$(dmpe)_2Ta(CO)_2Cl$ (3). To 9.46 g (15.2 mmol) of **1** dissolved in 150 ml of THF was added 78 ml of a 0.39 M sodium naphthalene solution (30.4 mmol) dropwise. The resulting brown solution of **2** was treated with an additional 39 ml of sodium naphthalene solution (15.2 mmol) over a 45-min period under a stream of CO. The CO was bubbled into the reaction mixture for an additional 2 h, giving a dark orange solution. After evaporation of the solvent, naphthalene was removed by sublimation (70 °C, 1 μm). Recrystallization of the residue from 3/1 toluene–hexane gave 4.0 g (7.0 mmol, 46%) of **3** as bright yellow crystals: ^{31}P NMR (1/1 toluene–THF) −22.7 ppm (s); IR (THF solution) ν_{CO} 1833 (vs), 1765 (s) cm^{-1}; mass spectrum *m/e* 572 $[^{12}C_{14}{}^{1}H_{32}{}^{35}Cl^{16}O_2{}^{31}P_4{}^{181}Ta]^+$, 516 $[P - 2CO]^+$.

Anal. Calcd for $C_{14}H_{32}ClO_2P_4Ta$: C, 29.37; H, 5.63. Found: C, 29.83; H, 5.53.

Reduction of 3. Dropwise addition of 2 equiv of a THF solution of sodium naphthalene to 263 mg of **3** in 20 ml of THF gave a deep red, highly air sensitive solution. Solution IR spectra (THF) indicated a strong, broad band at 1675 cm^{-1}. The solution was cooled to −196 °C and 1.1 equiv of DCl was condensed onto the frozen mass. Warming to 25 °C resulted in an orange solution with bands at 1833 and 1765 cm^{-1} and 1735 cm^{-1}, assignable to **3** and $(dmpe)_2Ta(CO)_2D$, respectively. On addition of a second equivalent of DCl, the band at 1735 cm^{-1} vanished and the bands attributable to **3** were enhanced. A similar experiment with HCl showed an additional broad band at 1590 cm^{-1} (ν_{TaH} of **7**)[10] after treatment with 1 equiv of acid. An analogous experiment monitored by ^{31}P NMR is illustrated in Figure 3.

In a similar experiment 272 mg of **3** in 25 ml of THF was treated with 2.1 equiv of sodium naphthalene. Addition of 80 μl of trifluoroacetic acid to the deep red solution resulted in an immediate lightening of the color to yellow. Evaporation of the solvent and removal of naphthalene as above left a yellow oily solid. Purification by preparative TLC (R_f 0.90, THF eluent, silica gel) and subsequent crystallization from benzene–heptane gave a yellow solid which is formulated as $(dmpe)_2Ta(CO)_2(CF_3CO_2)$ on the basis of its mass spectrum: *m/e* 650 $[^{12}C_{16}{}^{1}H_{32}{}^{19}F_3{}^{16}O_4{}^{31}P_4{}^{181}Ta]^+$, 622 $[P - CO]^+$, 594 $[P - 2CO]^+$; ^{31}P NMR (1/1 1,2-dimethoxyethane–THF) −15.8 ppm (s).

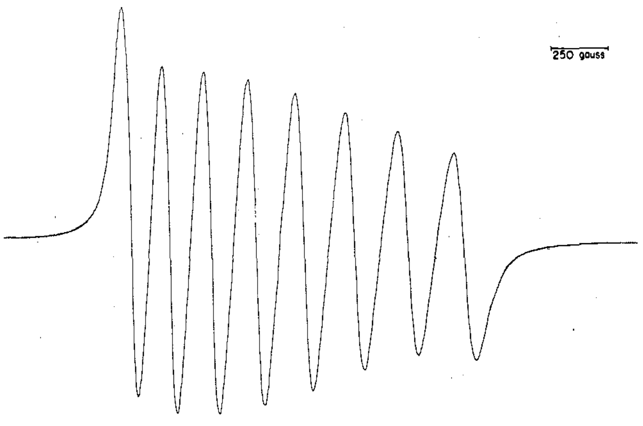


Figure 1. ESR spectrum of **1** in benzene at 25 °C.

(dmpe)$_2$Ta(CO)$_2$Br (5). A solution of 4 prepared as above from 321 mg (0.56 mmol) of 3 in 10 ml of THF and 1.12 mmol of sodium naphthalene was treated with 1.12 mmol of HBr at −196 °C. Warming to room temperature gave a yellow solution of **5**, which was isolated by evaporation of the solvent, sublimation of naphthalene, and crystallization of the residue by slow evaporation of a toluene extract. The yield of yellow crystals was essentially quantitative: ^{31}P NMR (1/1 toluene–THF) −19.1 ppm (s); IR (THF solution) ν_{CO} 1832 (vs), 1767 (s) cm^{-1}; mass spectrum m/e 618 $[^{12}C_{14}{}^{1}H_{32}{}^{81}Br^{16}O_2{}^{31}P_4{}^{181}Ta]^+$, 590 $[P - CO]^+$, 562 $[P - 2CO]^+$.

Anal. Calcd for $C_{14}H_{32}BrO_2P_4Ta$: C, 27.24; H, 5.23. Found: C, 26.49, H, 5.23.

(dmpe)$_2$Ta(CO)$_2$CH$_3$ (8). A solution of 0.37 mmol of 4 in 10 ml of THF was prepared as above from 209 mg of 3 and 0.75 mmol of sodium naphthalene. Treatment with 0.40 mmol of iodomethane at −196 °C and warming to 25 °C resulted in a yellow solution. Workup as above gave **8**: ^{1}H NMR (C_6D_6) 11.52 (q, 3, TaCH$_3$, J_{PCH} = 11.2 Hz), 8.76 (br, 24, PCH$_3$), 8.51 τ (br, 8, PCH$_2$); ^{31}P NMR (1/1 toluene–THF) −21.8 ppm (s); IR (THF solution) ν_{CO} 1823 (vs), 1760 (s) cm^{-1}; mass spectrum m/e 552 $[^{12}C_{15}{}^{1}H_{35}{}^{16}O_2{}^{31}P_4{}^{181}Ta]^+$, 537 $[P - Me]^+$, 524 $[P - CO]^+$, 496 $[P - 2CO]^+$.

Anal. Calcd for $C_{15}H_{35}O_2P_4Ta$: C, 32.61; H, 6.39. Found: C, 33.77; H, 6.57.

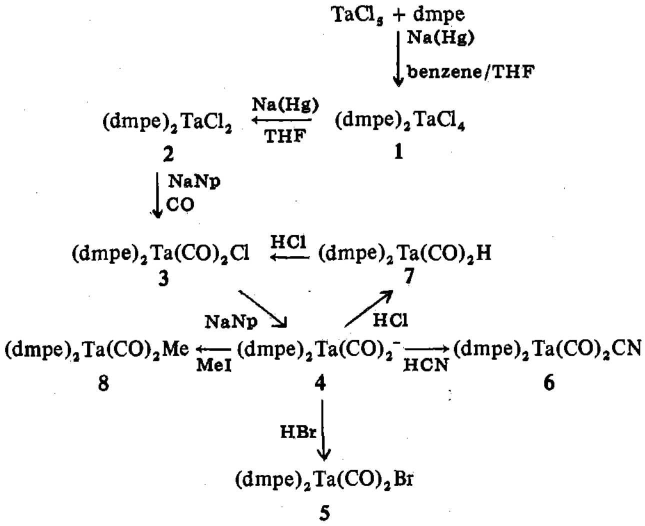
(dmpe)$_2$Ta(CO)$_2$CN (6). To 0.49 mmol of 4 in 25 ml of THF, prepared as above, was added 2.45 mmol of HCN at −196 °C. The mixture was warmed to 25 °C and stirred for 1 h. Evaporation of the solvent and removal of naphthalene by sublimation left a greenish residue. Purification was effected by preparative TLC (silica gel, THF eluent, R_f 0.7) and recrystallization from benzene–heptane: ^{31}P NMR (1/1 toluene–THF) −13.3 ppm (s); IR (THF solution) ν_{CO} 1842 (vs), 1783 (s), and (Nujol mull) ν_{CN} 2078 (m) cm^{-1}; mass spectrum m/e 563 $[^{12}C_{15}{}^{1}H_{32}{}^{14}N^{16}O_2{}^{31}P_4{}^{181}Ta]^+$, 535 $[P - CO]^+$, 507 $[P - 2CO]^+$.

Anal. Calcd for $C_{15}H_{32}NO_2P_4Ta$: C, 31.97; H, 5.72. Found: C, 33.73; H, 6.06.

Results

Treatment of a 1:2 TaCl$_5$–dmpe mixture in benzene containing 15% THF with sodium amalgam gives a deep blue solution from which (dmpe)$_2$TaCl$_4$ (**1**) can be isolated in good yield. Larger proportions of THF lead to further reduction (vide infra); smaller amounts result in inconveniently long reaction times. The ESR spectrum of **1** in Figure 1 exhibits an eight-line pattern at g = 1.901 due to the ^{181}Ta ($I = {}^7/_2$) hyperfine interaction. ^{31}P hyperfine is not observed; consequently, the stereochemistry is undetermined, although presumably similar to that of (diars)$_2$TaCl$_4$ (diars = *o*-phenylenebis(dimethylarsine)), which has been isolated as an impure solid and assigned a dodecahedral structure on the basis of visible and infrared spectra.[11] **1** is sufficiently volatile for mass spectral measurements; a parent ion is observed with an isotope envelope in close agreement with that calculated for a TaCl$_4$ containing fragment. In contrast to TaCl$_5$,[12] **1** is stable in refluxing ethereal solvents and the solid may be handled for moderate periods in the air. Consequently, this compound constitutes a convenient starting material, although obviously limited to the Ta(dmpe)$_2$ system.

Scheme I



Np = naphthalene

Reactions of **1** with alkyllithium reagents are extremely complex but give, primarily, reduced products. Thus, excess methyllithium containing lithium bromide affords principally (dmpe)$_2$TaBr$_2$ (identified via mass spectroscopy). In no case could Ta(IV) alkyls be detected.

Reduction of **1** in THF with Na/Hg or sodium naphthalene affords red-brown, extremely air sensitive, (dmpe)$_2$TaCl$_2$ (**2**), which, on the basis of its high solubility, is likely the trans isomer. Prolonged reaction times led to a complex mixture of products which in out hands proved unseparable. No evidence for the presumed intermediate, (dmpe)$_2$TaCl$_3$, could be found. Addition of 1 equiv of sodium naphthalene to **1** resulted in a deep-green solution; however, evaporation of the solvent resulted only in a mixture of **1** and **2**. Similar results were obtained with deficiencies of Na/Hg. Mixtures of **1** and **2** in benzene, although green in appearance, showed only a superposition of the absorptions of **1** and **2** in their visible spectra.

As shown in Scheme I, addition of 1 equiv of sodium naphthalene in the presence of 1 atm of CO to solutions of **2** (conveniently generated in situ from **1** and sodium naphthalene) gives (dmpe)$_2$Ta(CO)$_2$Cl (**3**). Addition of 2 equiv of sodium naphthalene to **3** gives a deep red solution, presumably containing Na[(dmpe)$_2$Ta(CO)$_2$] (**4**). Although **4** has not been isolated, its formulation is consistent with the chemistry outlined in Scheme I. Further, the low value of ν_{CO} (1675 vs. ca. 1800 cm^{-1} for **3**) is indicative of an anionic species. The breadth of the band and solvent interference preclude any stereochemical assignment solely on the basis of infrared data. When monitored by ^{31}P NMR (Figure 3) the single resonance of **3** is converted to two approximate doublets, attributable to **4**, after addition of sodium naphthalene. This is consistent with a partially resolved AA′XX′ pattern (δ_A = −20.1 and δ_X = −5.3 ppm) anticipated for the cis structure in Figure 2. The neutral, 17-electron complex (dmpe)$_2$Ta(CO)$_2$ could not be detected during the reduction of **3**, either via IR or ESR spectroscopy.

Treatment of **4** with 2 equiv of anhydrous HCl, HBr, or HCN gave **3**, (dmpe)$_2$Ta(CO)$_2$Br (**5**), and (dmpe)$_2$Ta(CO)$_2$CN (**6**), respectively, in essentially quantitative yields. Infrared monitoring experiments established these reactions proceed through the previously reported hydride[10] (ν_{CO} = 1753 cm^{-1}, ν_{TaH} = 1590 cm^{-1}), (dmpe)$_2$Ta(CO)$_2$H (**7**). As shown in Figure 3, protonation of **4** with CF$_3$CO$_2$H affords **7** (by comparison with an authentic sample[10]) contaminated by a component with a single resonance at −15.8 ppm. This species

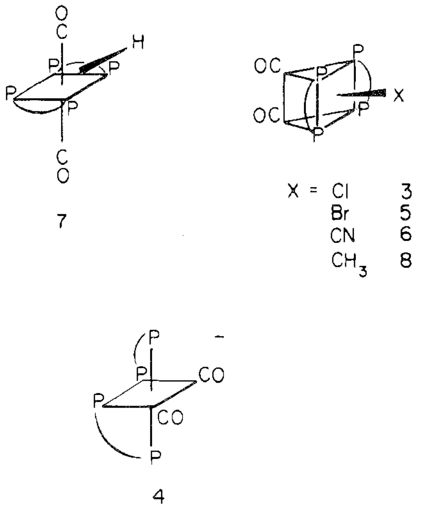


Figure 2. Proposed geometries of $(dmpe)_2Ta(CO)_2X$ and $Na[(dmpe)_2Ta(CO)_2]$.

may be isolated by preparative TLC and is formulated as $(dmpe)_2Ta(CO)_2(CF_3CO_2)$. The mode of binding of the trifluoroacetate group is undetermined. **4** is sufficiently nucleophilic to react with iodomethane, generating $(dmpe)_2Ta(CO)_2Me$ (**8**).

The seven-coordinate derivatives **3**, **5**, **6**, and **8** all show a single ^{31}P NMR resonance in the temperature range +90 to −80 °C. Additionally, the methyl resonance in the ^1H NMR of **8** appears as a well-resolved quintet over the same temperature interval. Two carbonyl bands (ca. 1830 and 1760 cm^{-1}) are observed in all cases; the band at higher frequency is the more intense; the intensity ratio of 1.61 is largely invariant. These data strongly suggest the structure indicated in Figure 2 (vide infra), i.e., one in which the phosphorus atoms are equivalent and the carbonyls are in a mutually cis arrangement.

We note **3** is kinetically inert; dissociation of halide does not occur readily. Thus, **3** does not react appreciably with thallium fluoroborate (silver ion is instantly reduced) in acetone at 25 °C or in THF at 100 °C either in the presence or absence of added ligands (CO or C_2H_4).

Discussion

Three idealized geometries are usually considered for seven-coordinate complexes: the D_{5h} pentagonal bipyramid, C_{3v} monocapped octahedron, and the C_{2v} monocapped trigonal prism.[1,4] Examples which are close to the idealized geometries are known for all three, although many are grossly distorted and some appear to be intermediate.[4f] Within these constraints the only geometry consistent with the spectroscopic data for **3**, **5**, **6**, and **8** is the C_{2v} structure in Figure 2. This assignment is supported by comparison with the isoelectronic $[Mo(diars)_2(CO)_2Cl]I_3$, whose structure has been determined by x-ray methods and is analogous.[13] Furthermore, $[Mo(dmpe)_2(CO)_2I]I$, prepared by Connor et al.,[14] has been suggested to have a similar structure.

Under the proposed C_{2v} symmetry the carbonyl groups are equivalent; this allows an accurate estimate of ∠CO–Ta–CO on the basis of intensity ratios.[15] For **3** an angle of 74 ± 2° is computed, in good agreement with 67.7° found for $[Mo(diars)_2(CO)_2Cl]I_3$.[13]

The hydride **7**, first prepared by Tebbe,[10] has a monocapped octahedral structure by x-ray methods,[16] as in Figure 2. The hydride ligand, although unlocated, is presumed to be the capping ligand on the basis of observed distortions from a D_{2h} geometry. Inasmuch as hydride and methyl are both good σ donors, the difference in structure between **7** and **8** appears to be a result of the size of the capping ligand. The inability of the molecule to accommodate the bulkier methyl group in the relatively congested triangular face is apparently responsible for the change in geometry. Conceptually, **7** and **8** are related by motion of the carbonyl in the capped face of **7** through the P_4 plane (via a pentagonal bipyramidal structure). We note **8** can arise from simple methylation of an edge of the anion **4** accompanied by a minor distortion and suggest **7** may be derived by protonation in a similar fashion, followed by the rearrangement described. However, protonation or methylation at −70 °C gives **7** and **8** directly; no intermediates of different geometry were detectable by ^{31}P NMR (Figure 3).

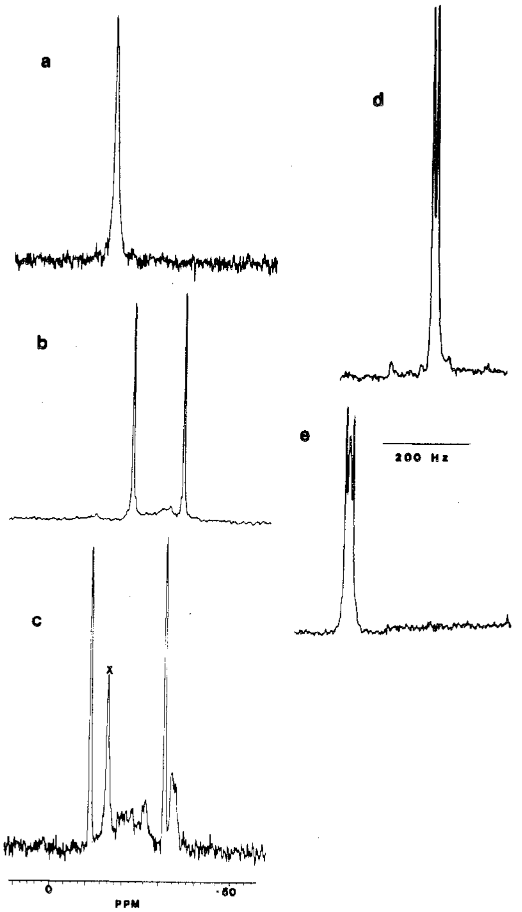


Figure 3. The 40.5 MHz ^{31}P NMR (1/1 1,2-dimethoxyethane–THF) of (a) $(dmpe)_2Ta(CO)_2Cl$, (b) after addition of 2.1 equiv of sodium naphthalene, followed by (c) addition of 1.1 equiv of trifluoroacetic acid. The high-field resonances in (b) and (c) are illustrated in (d) and (e), respectively, with an expanded scale. The resonance marked X in (c) corresponds to $(dmpe)_2Ta(CO)_2(CF_3CO_2)$.

Inasmuch as **3**, **5**, **6**, **8**, $[Mo(diars)_2(CO)_2Cl]I_3$, and $[Mo(dmpe)_2(CO)_2I]I$ all have their carbonyl ligands on the unique edge of the capped trigonal prism, it would appear that good π-accepting ligands prefer these positions. No discrimination on an electronic basis is observed at the capping site; i.e., halide (π donor), methyl (σ donor), and cyanide (π acceptor) all reside at this position. This observation suggests either there is, in fact, little electronic difference between the capping and quadrilateral face sites, in which case the structure is determined on steric grounds, or the electronic preference of dmpe for the quadrilateral face is overwhelming. In view of the range of capping ligands, the latter seems unlikely.

Recent site preference predictions derived from MO arguments[4g] are in agreement with the structures proposed for **3** and **5**. To the extent that cyanide is a good π acceptor,[17] **6** violates these proposed preference rules. We note **7** is also in violation of these predictions. However, all of these compounds have bidentate ligands which may obscure electronic site preferences.[4g]

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Registry No. **1**, 61916-34-5; **2**, 61916-35-6; **3**, 61916-36-7; **4**, 61916-37-8; **5**, 61966-89-0; **6**, 61916-23-2; **7**, 50600-13-0; **8**, 61916-24-3; $(dmpe)_2Ta(CO)_2D$, 61916-25-4; $(dmpe)_2Ta(CO)_2(CF_3CO_2)$, 61916-26-5; $TaCl_5$, 7721-01-9.

References and Notes

(1) (a) E. L. Muetterties and L. J. Guggenberger, *J. Am. Chem. Soc.*, **96**, 1748 (1974); (b) E. L. Muetterties, *Tetrahedron*, **30**, 1595 (1974).
(2) (a) J. S. Wood, *Prog. Inorg. Chem.*, **16**, 227 (1972); (b) E. L. Muetterties and R. A. Schunn, *Q. Rev., Chem. Soc.*, **20**, 245 (1966); (c) B. A. Frenz and J. A. Ibers, *MTP Int. Rev. Sci.: Phys. Chem., Ser. One*, **11**, 33 (1972); (d) A. R. Rossi and R. Hoffman, *Inorg. Chem.*, **14**, 365 (1975).
(3) L. H. Pignolet, R. A. Lewis, and R. H. Holm, *J. Am. Chem. Soc.*, **93**, 360 (1971).
(4) (a) E. L. Muetterties and C. M. Wright, *Q. Rev., Chem. Soc.*, **21**, 109 (1967); (b) R. J. Gillespie, *Can. J. Chem.*, **38**, 818 (1960); (c) D. Britton, *ibid.*, **41**, 1632 (1963); (d) T. A. Claxton and G. C. Benson, *ibid.*, **44**, 157 (1966); (e) H. B. Thompson and L. S. Bartell, *Inorg. Chem.*, **7**, 488 (1968); (f) J. K. Kouba and S. S. Wreford, *ibid.*, **15**, 1463 (1976); (g) R. Hoffmann, B. F. Beier, E. L. Muetterties, and A. R. Rossi, *Inorg. Chem.*, **16**, 511 (1977).
(5) Seven-coordinate tantalum(I) complexes of the general formula $Ta(CO)_6X$ and more substituted derivatives have been reported in ref 6. The structures of these compounds were undetermined. In this regard, we note that the published infrared data on the $Ta(CO)_6$ derivatives in ref 6 are compatible with a C_{2v} structure based on a monocapped trigonal prism.
(6) A. Davison and J. E. Ellis, *J. Organomet. Chem.*, **36**, 113 (1972).
(7) A. J. Leffler and R. Penque, *Inorg. Synth.*, **12**, 187 (1970).
(8) S. A. Butter and J. Chatt, *Inorg. Synth.*, **15**, 185 (1974).
(9) J. Chatt and H. R. Watson, *J. Chem. Soc.*, 2545 (1962).
(10) F. N. Tebbe, *J. Am. Chem. Soc.*, **95**, 5823 (1973).
(11) R. L. Deutscher and D. L. Kepert, *Inorg. Chem.*, **9**, 2305 (1970).
(12) D. L. Kepert, "The Early Transition Metals", Academic Press, New York, N.Y., 1972.
(13) M. G. B. Drew and J. C. Wilkins, *J. Chem. Soc., Dalton Trans.*, 2664 (1973).
(14) (a) J. A. Connor, G. K. McEwen, and C. J. Rix, *J. Less-Common Met.*, **36**, 207 (1974); (b) J. A. Connor, G. K. McEwen, and C. J. Rix, *J. Chem. Soc., Dalton Trans.*, 589 (1974).
(15) W. Beck, A. Melnikoff and R. Stahl, *Chem. Ber.*, **99**, 3721 (1966).
(16) P. Meakin, L. J. Guggenberger, F. N. Tebbe, and J. P. Jesson, *Inorg. Chem.*, **13**, 1025 (1974).
(17) (a) See, for example, L. Malatesta and S. Cenini, "Zerovalent Compounds of Metals", Academic Press, New York, N.Y., 1974, and references therein; (b) A. G. Sharpe and B. M. Chadwick, *Adv. Inorg. Chem. Radiochem.*, **8**, 84 (1966).

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Comparative Geometry of $Rh(\mu\text{-}Cl)_2Rh$ and $Rh(\mu\text{-}H)(\mu\text{-}Cl)Rh$ Bridges. Crystal Structure of $[\eta^5\text{-}C_5Me_5RhCl]_2(\mu\text{-}Cl)_2$ and Its Relationship to $[\eta^5\text{-}C_5Me_5RhCl]_2(\mu\text{-}H)(\mu\text{-}Cl)$

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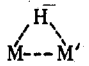
A single-crystal x-ray diffraction study has been performed on the complex di-μ-chloro-dichlorobis(pentamethylcyclopentadienyl)dirhodium, $[\eta^5\text{-}C_5Me_5RhCl]_2(\mu\text{-}Cl)_2$. This species crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ [C_{2h}^5; No. 14] with $a = 8.375$ (1) Å, $b = 9.228$ (2) Å, $c = 15.651$ (2) Å, $\beta = 106.70$ (1)°, and $V = 1158.6$ (3) $Å^3$ at 22 °C. Observed and calculated densities are 1.764 (10) and 1.772 g cm^{-3} for mol wt 618.08 and $Z = 2$. Diffraction data were collected with a Syntex $P2_1$ automated diffractometer. The structure was solved by a combination of Patterson, Fourier, and least-squares refinement techniques. Final discrepancy indices are $R_F = 2.57\%$ and $R_{wF} = 3.47\%$ for 1513 symmetry-independent reflections in the range $4° < 2\theta \leq 45°$ (Mo Kα radiation). The molecule has crystallographic C_i ($\bar{1}$) symmetry with a planar $Rh(\mu\text{-}Cl)_2Rh$ bridge in which Rh···Rh = 3.7191 (6) Å, Rh–ClB = 2.452 (1) and 2.465 (1) Å, Rh–ClB–Rh′ = 98.29 (3)°, and ClB–Rh–ClB′ = 81.71 (3)°. The central $Rh(\mu\text{-}Cl)_2Rh$ bridge is compared with the $Rh(\mu\text{-}Cl)(\mu\text{-}H)Rh$ bridge in $[\eta^5\text{-}C_5Me_5RhCl]_2(\mu\text{-}Cl)(\mu\text{-}H)$ with a view toward assessing bonding characteristics in a nonstressed $M(\mu_2\text{-}H)M$ system within a binuclear species.

Introduction

The structural characterization of transition metal complexes containing bridging hydride ligands has been an area of considerable interest for the last few years. We have recently summarized the results of x-ray (and neutron) diffraction studies on these species.[1] It is now generally agreed that a bent $M(\mu_2\text{-}H)M'$ system contains a "closed" two-electron three-center bond—i.e., that there is both direct metal–hydrogen bonding and a direct metal–metal bonding interaction within this system. We have suggested that such a system be represented by I.



I

Mason and Mingos[2] have surveyed the geometry of binuclear and polynuclear complexes with bridging ligands and have noted that "electron-deficient" species (i.e., those with bridging ligands with only one pair of electrons available for bonding—hydride, alkyl, and aryl ligands, inter alia) have shorter metal–metal distances than do "electron-precise" species (i.e., those containing bridging ligands with at least two electron pairs available for bonding).

However, the only direct comparisons of complexes with bridging hydride ligands with their corresponding "electron-precise" analogues involves a trio of trinuclear osmium carbonyl species[2,3]—viz., $Os_3(CO)_{10}(\mu\text{-}H)_2$ (II), $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}SEt)^4$ (III), and $Os_3(CO)_{10}(\mu\text{-}OMe)_2$ (IV).

While there is an obvious lengthening of the bis(μ_2-bridged) osmium–osmium vector as hydride ligands are successively replaced by "electron-precise" ligands, the bond under investigation may be subject to some additional constraints from the bridging $-Os(CO)_4-$ moiety. Thus, in order to isolate the effects of replacement of the μ_2-hydride ligand from other