Multiple Metal-Carbon Bonds. 15.[1] Octahedral Alkylidene Complexes of Niobium and Tantalum by Ligand-Promoted α Abstraction

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Abstract: Complexes of the type $M(CH_2R)_2X_3$ (M = Nb or Ta; R = CMe_3, Ph, or $SiMe_3$; X = Cl or Br) react with donor ligands to give a mixture of *cis,mer-* and *trans,mer-*$M(CHR)L_2X_3$ (L = PMe_3, $PPhMe_2$, PPh_2Me, py, THF) in the presence of two or more L, $[M(CHCMe_3)LX_3]_2$ in the presence of one L (a phosphine), or *mer-*$M(CHCMe_3)(L-L)X_3$ in the presence of L-L (L-L = dmpe, diars, diphos, tmeda, bpy). The rate of this ligand promoted α-hydrogen abstraction reaction varies qualitatively in the order R = CMe_3 > Ph ≈ $SiMe_3$, X = Br > Cl, L = PMe_3 > $PPhMe_2$ > PPh_2Me > L-L (except dmpe), and solvent = dichloromethane ≈ chloroform > pentane. The most likely immediate precursor to $M(CHR)L_2X_3$ is seven-coordinate $M(CH_2R)_2L_2X_3$. Transient, five-coordinate $M(CHR)LX_3$ forms at a rate which is rapid on the NMR time scale from $[M(CHCMe_3)LX_3]_2$ or $M(CHR)L_2X_3$. This is believed to be the reason why *cis,mer-* and *trans,mer-*$M(CHR)L_2X_3$ interconvert so readily. NMR and IR data for all complexes ($\delta(C_\alpha)$ ca. 250-275, J_{CH_α} = 70-100 Hz, ν_{CH_α} = 2400-2700 cm^{-1}) suggest that the metal attracts electron density from the CH_α bond. Therefore the coordination sphere probably is distorted significantly from an octahedron in all cases.

Introduction

Intramolecular abstraction of one alkyl ligand's α-hydrogen atom by another alkyl ligand in certain types of Nb(V) and Ta(V) alkyl complexes (especially neopentyl complexes[3]) yields stable alkylidene complexes.[4] Among the geometries and coordination numbers which are known so far, the octahedron is notably absent. Since phosphines are known to be compatible with what are expected to be nucleophilic alkylidene ligands, and a crowded coordination sphere is one prerequisite for α abstraction, we attempted to induce α abstraction in MR_2X_3 complexes by adding tertiary phosphine ligands. This approach was successful and yielded a large class of octahedral neopentylidene complexes of the type $M(CHCMe_3)L_2X_3$ (M = Nb or Ta; X = Cl or Br) as well as an analogous benzylidene and a trimethylsilylmethylidene complex. Later we found that nitrogen donor ligands (e.g., tmeda, py) and even tetrahydrofuran would induce α abstraction to give analogous octahedral neopentylidene complexes. Since THF is quite labile, the THF complexes are excellent starting materials for all other octahedral complexes as well as other types of neopentylidene complexes which cannot be prepared directly by an α-abstraction reaction. In this paper we give the complete details of the preparation and characterization of octahedral alkylidene complexes, discuss their solution chemistry, and attempt to determine how they are formed.

Results

Preparation of Octahedral Alkylidene Complexes. Preparation of $M(CHCMe_3)L_2X_3$ (M = Nb, Ta; L = a Tertiary Phosphine; X = Cl, Br). When 1 equiv of PMe_3 is added to $Ta(CH_2CMe_3)_2Cl_3$[3] in pentane, slightly soluble orange needles with the composition $Ta(CH_2CMe_3)_2(PMe_3)Cl_3$ crystallize from solution. They can be isolated and recrystallized but are not stable thermally in solution. In the presence of another equivalent of PMe_3 they redissolve in approximately 30 min to give a purple solution which deposits a purple oil after several hours. A fibrous crystalline product with the composition $Ta(CHCMe_3)(PMe_3)_2Cl_3$ can be obtained from ether/pentane solution. Similar (but slower) reactions employing $PPhMe_2$ and PPh_2Me yield analogous complexes which crystallize directly from the reaction mixture. In each case, 1 equiv of neopentane forms. Therefore the overall reaction is that shown in eq 1. The reaction between $Ta(CH_2CMe_3)_2Cl_3$ and PPh_3 is very slow (as judged by the rate of formation of neopentane), and no analogous product was ever observed. The reaction of $Ta(CH_2CMe_3)_2Br_3$ with tertiary phosphines is noticeably faster but otherwise closely analogous to the reactions involving $Ta(CH_2CMe_3)_2Cl_3$.

$$Ta(CH_2CMe_3)_2X_3 + 2L \xrightarrow{\text{pentane}} Ta(CHCMe_3)L_2X_3 + CMe_4 \quad (1)$$

X = Cl, Br; L = PMe_3, $PPhMe_2$, PPh_2Me

Niobium complexes are not formed as cleanly. When PMe_3 is added to $Nb(CH_2CMe_3)_2Cl_3$ in pentane, the initially red-orange solution turns red and then purple and a brown-green solid forms, all within a few seconds at 25 °C. If the solid is quickly filtered off, $Nb(CHCMe_3)(PMe_3)_2Cl_3$ crystallizes out in ca. 60% yield. Much lower yields are obtained if the solution is not filtered immediately after the PMe_3 is added. $Nb(CHCMe_3)(PPhMe_2)_2Cl_3$ can be prepared similarly, but $Nb(CHCMe_3)(PPh_2Me)_2Cl_3$ was never obtained in a pure state.

The rate of this α-abstraction reaction depends on both the solvent and the halide. For a given type of phosphine the reaction is noticeably faster in chloroform or dichloromethane than in pentane, and a bromide complex always reacts faster than a chloride complex.

All cryoscopic molecular weight measurements for these complexes are lower than calculated values. For example, the molecular weight of $Ta(CHCMe_3)(PMe_3)_2Cl_3$ was found to be 377 (calculated 510). A reasonable explanation is that PMe_3 dissociates in solution. We later present more evidence that this is, in fact, a general property of complexes which contain monodentate ligands.

$[M(CHCMe_3)LX_3]_2$ (M = Nb, Ta; L = a Tertiary Phosphine; X = Cl, Br). If only 1 equiv of L is added to $Ta(CH_2CMe_3)_2Cl_3$, the initially formed $Ta(CH_2CMe_3)_2(PMe_3)Cl_3$ first disproportionates to $Ta(CHCMe_3)(PMe_3)_2Cl_3$ and $Ta(CH_2CMe_3)_2Cl_3$ (by ^1H NMR) and then a deep red complex with the composition $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$ slowly forms (eq 2). A cryoscopic molecular weight measurement showed it to be a dimer. Experiments using different phosphine ligands or Nb gave analogous results. We have also prepared one bromide analogue, red [Ta-

$$M(CH_2CMe_3)_2LCl_3 \rightarrow 0.5M(CHCMe_3)L_2Cl_3 + 0.5M(CH_2CMe_3)_2Cl_3 \rightarrow 0.5[M(CHCMe_3)LCl_3]_2 \quad (2)$$

M = Ta, L = PMe_3, $PPhMe_2$, PPh_2Me

M = Nb, L = PMe_3, $PPhMe_2$

(1) Part 14. Sharp, P. R.; Schrock, R. R. *J. Organomet. Chem.* **1979**, *171*, 43-51.
(2) Camille and Henry Dreyfus Teacher-Scholar Grant Recipient, 1978.
(3) Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210-3222.
(4) Schrock, R. R. *Acc. Chem. Res.* **1978**, *12*, 98-104.

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$(CHCMe_3)(PMe_3)Br_3]_2$. Any of these dimers is rapidly and quantitatively converted into the monomeric species by adding L. If L is PMe_3, this reaction can be reversed, partly due to the fact that PMe_3 is so volatile and partly due to the fact that $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$ is considerably less soluble than $Ta(CHCMe_3)(PMe_3)_2Cl_3$ in toluene; for example, $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$ will crystallize out of concentrated solutions of $Ta(CHCMe_3)(PMe_3)_2Cl_3$. These data establish that the monomeric and dimeric species are in equilibrium (eq 3).

$$M(CHCMe_3)L_2X_3 \underset{+L}{\overset{-L}{\rightleftharpoons}} 0.5[M(CHCMe_3)LX_3]_2 \quad (3)$$

A mixture of $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$ and $[Ta(CHCMe_3)(PMe_3)Br_3]_2$ in $CDCl_3$ shows only one broad neopentylidene α-proton signal in the 30 °C ^1H NMR spectrum at ca. τ 6.5. After cooling the sample in the probe, we see many α-proton signals in that region. We propose these signals are due to α protons in all possible $Ta_2(CHCMe_3)_2(PMe_3)_2Cl_xBr_y$ species; i.e., halide exchange between transient five-coordinate $M(CHCMe_3)LX_3$ complexes must be fast.

The $[Ta(CHCMe_3)LX_3]_2$ complexes are quite stable in solution but the analogous Nb species, $[Nb(CHCMe_3)LCl_3]_2$ (L = PMe_3 or $PPhMe_2$), decompose in several hours in toluene or chloroform to as yet unidentified products.

$M(CHR)L_2X_3$ (R = Ph, $SiMe_3$; L = a Tertiary Phosphine). $Ta(CH_2SiMe_3)_2Cl_3$ does not react readily with PMe_3 in pentane, but it does in chloroform to give green $Ta(CHSiMe_3)(PMe_3)_2Cl_3$. Since a chlorinated solvent is required for a rapid rate, α abstraction from CH_2SiMe_3 must be considerably slower than it is from CH_2CMe_3.

Adding PMe_3 to $Ta(CH_2Ph)_2Cl_3$ in benzene gives an isolable adduct, $Ta(CH_2Ph)_2(PMe_3)Cl_3$. Unlike $Ta(CH_2CMe_3)_2(PMe_3)Cl_3$, $Ta(CH_2Ph)_2(PMe_3)Cl_3$ is relatively stable in toluene, even at 50 °C. However, if two more equivalents of PMe_3 are added, and the mixture is warmed to ca. 50 °C for 1 h, green $Ta(CHPh)(PMe_3)_2Cl_3$ can be isolated in 80% yield (eq 4). An

$$Ta(CH_2Ph)_2X_3 \xrightarrow[>2PMe_3]{\text{benzene, 50 °C, 1 h}} Ta(CHPh)(PMe_3)_2X_3 + \text{toluene} \quad (4)$$

X = Cl, Br

identical procedure employing $Ta(CH_2Ph)_2Br_3$ gave emerald green $Ta(CHPh)(PMe_3)_2Br_3$ (70% yield) after 1.5 h at 25 °C. In each case 1.0 equiv of toluene was found in the reaction volatiles. These complexes are less soluble in toluene than their neopentylidene analogues, but they are nicely soluble (although not as stable) in chloroform or dichloromethane.

The above reaction fails completely or the yield of $Ta(CHPh)(PMe_3)_2X_3$ is low if <2 equivalents of PMe_3 are added to $Ta(CH_2Ph)_2X_3$. We also find that although the PMe_3 ligands are labile in $Ta(CHPh)(PMe_3)_2Cl_3$, we have seen no evidence for $[Ta(CHPh)(PMe_3)X_3]_2$. Therefore, we assume it, or more likely "$Ta(CHPh)(PMe_3)X_3$", is unstable with respect to formation of stilbenes (see later).

$M(CHCMe_3)(L\text{-}L)X_3$ (L-L = dmpe, diphos, diars, tmeda, bpy). Diphos, diars, tmeda, or bipy do not react with $Ta(CH_2CMe_3)_2Cl_3$ in pentane. However, in dichloromethane all react readily to give monomeric neopentylidene complexes (eq 5). Bromide complexes

$$Ta(CH_2CMe_3)_2X_3 + L\text{-}L \xrightarrow{CH_2Cl_2} Ta(CHCMe_3)(L\text{-}L)X_3 + CMe_4 \quad (5)$$

X = Cl, L-L = dmpe, diphos, diars, tmeda, bpy

X = Br, L-L = dmpe, diphos

can be prepared analogously, and we have prepared one niobium example, $Nb(CHCMe_3)(dmpe)Cl_3$. Cryoscopic molecular weight measurements in several cases confirm that these complexes are monomers. The diphos complex, and especially the bpy complex, are considerably less soluble than the others.

Dmpe (1,2-bis(dimethylphosphino)ethane) reacts readily with $Ta(CH_2CMe_3)_2Cl_3$ in dichloromethane to give $Ta(CHCMe_3)(dmpe)Cl_3$. This complex is indefinitely stable only in chloroform or dichloromethane. In diethyl ether a white powder slowly forms. If one attempts to prepare $Ta(CHCMe_3)(dmpe)Cl_3$ in pentane or diethyl ether, the same (by IR) white powder forms. Since the reactions of this white powder are typical of a compound which contains a neopentylidene ligand (see Experimental Section), we believe it is a polymeric form containing bridging dmpe ligands (eq 6). Since complexes containing other chelating ligands do not behave this way, there is a slight chance that the reaction to give the white polymer involves dmpe in a more complex manner.

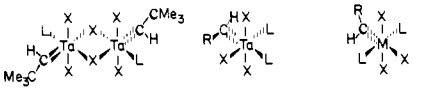
$$Ta(CHCMe_3)(dmpe)Cl_3 \xrightarrow{\text{ether}} (1/x)[Ta(CHCMe_3)(dmpe)Cl_3]_x \quad (6)$$

$M(CHCMe_3)L_2X_3$ (L = THF, py). THF induces loss of neopentane from $M(CH_2CMe_3)_2X_3$ in diethyl ether to give violet crystals of $M(CHCMe_3)(THF)_2X_3$ (M = Nb, X = Cl; M = Ta, X = Cl, Br). These complexes can be crystallized at low temperature from ether and stored at −30 °C, but at room temperature they slowly decompose. Often we simply prepare them in situ as needed by adding THF to an ether solution of $M(CH_2CMe_3)_2X_3$. In the presence of a slight excess of THF they appear to be indefinitely stable.

The $M(CHCMe_3)(THF)_2X_3$ complexes are important additions to this class of complexes for three reasons. First, the yields are high for Nb and quantitative for Ta. (In the case of niobium apparent reduction of the metal when a phosphine ligand is added to $Nb(CH_2CMe_3)_2Cl_3$ is often a serious problem; see above.) Second, the THF ligands are labile and readily displaced. For example, we have prepared many of the phosphine complexes from the THF complexes. Third, we can also prepare other types of complexes which cannot be prepared efficiently by a direct α-abstraction route. Two examples are $Nb(\eta^5\text{-}C_5H_5)(CHCMe_3)Cl_2$ and $Nb(\eta^5\text{-}C_5Me_5)(CHCMe_3)Cl_2$.[3]

$Ta(CH_2CMe_3)_2Cl_3$ reacts with pyridine in dichloromethane to give purple crystals of $Ta(CHCMe_3)(py)_2Cl_3$. This complex is more stable than $Ta(CHCMe_3)(THF)_2Cl_3$ since the pyridine ligands probably coordinate more strongly than THF.

IR and NMR Data and Structures. The ^{13}C NMR spectrum of $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$ shows a double doublet at 276 ppm (J_{CP} = 7 Hz, J_{CH_α} = 101 Hz) due to the neopentylidene α-carbon atom. This chemical shift and coupling constant are fairly typical of electron-deficient alkylidene complexes.[4] The structure of this complex is known[5] and is shown schematically below (**1**). The



1 **2** **3**

two most important features which we should note here are that the neopentylidene $H_\alpha\text{-}C_\alpha\text{-}C_\beta$ plane contains the X-Ta-X axis (i.e., the neopentylidene ligand "lies along the X-Ta-X axis"), and the phosphine ligand is cis to the neopentylidene ligand. Since the π bond is likely to be reasonably strong,[4] we assume that the alkylidene ligand in all complexes lies along one of the axes which is orthogonal to that containing M and C_α.

The ^{13}C NMR spectrum of $Ta(CHCMe_3)(dmpe)Cl_3$ shows that the neopentylidene α-carbon atom is coupled to two phosphorus nuclei. One appears to be cis to C_α (J_{CP} = 13 Hz) and the other trans to C_α (J_{CP} = 23 Hz). This is confirmed by the fact that there are only two types of dmpe methyl groups in the ^{13}C (or ^1H) NMR spectrum and two types of phosphorus nuclei ($J_{PP'} \approx$ 10 Hz characteristic of cis P and P') in the $^{31}P\{^1H\}$ NMR spectrum. The structure must be cis,*mer* (**2** or the one with the alkylidene ligand rotated by 180 °C). The NMR data for the diphos, bpy, tmeda, and diars complexes suggest that they also have the cis,*mer* structure, **2**.

The NMR spectra of the species containing monodentate donor ligands must be done at low temperature to slow down ligand exchange (see next section). The $^{13}C\ \{^1H\}$ NMR spectrum of $Ta(CHPh)(PMe_3)_2Cl_3$ in $CDCl_3$ (the relevant parts are shown

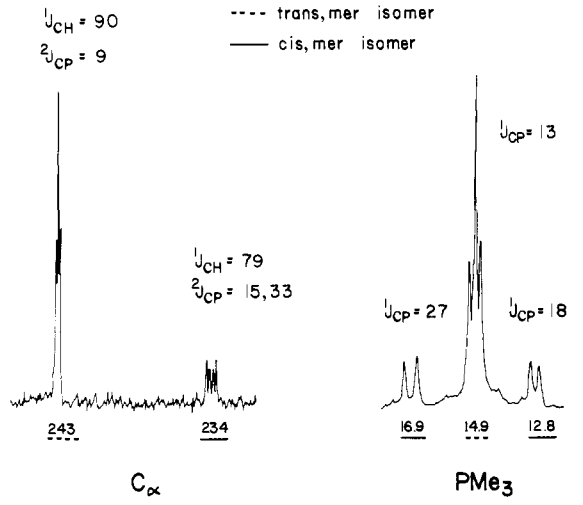


Figure 1. The 67.89-MHz $^{13}C\{^1H\}$ NMR spectrum of Ta(CHPh)-$(PMe_3)_2Cl_3$ in $CDCl_3$ at −40 °C (alkylidene C_α and phosphine methyl carbon atoms only).

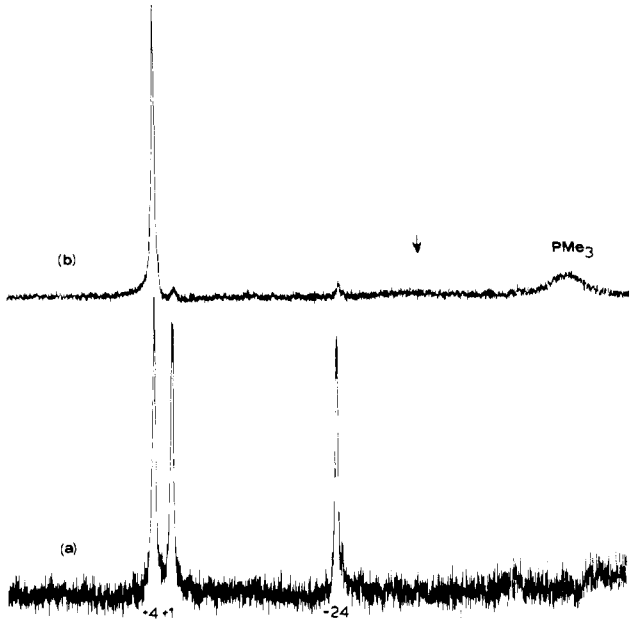


Figure 2. The 36.43-MHz $^{31}P\{^1H\}$ NMR spectrum of Ta(CHPh)-$(PMe_3)_2Cl_3$ in CH_2Cl_2 at −47 °C: (a) without added PMe_3; (b) with ca. 2 equiv of PMe_3 (arrow indicates approximate position of one rapidly exchanging PMe_3 ligand in $Ta(CHPh)(PMe_3)_3Cl_3$; see Figure 4).

in Figure 1) is typical of complexes of this type. One of the two species present is clearly of type **2** (J_{CP} = 15 Hz, $J_{CP'}$ = 33 Hz). The other contains equivalent phosphine ligands (J_{CP} = 9 Hz) and therefore must be trans,*mer* (type **3**). The ^{31}P NMR spectrum of $Ta(CHPh)(PMe_3)_2Cl_3$ (Figure 2a) is also consistent with a mixture of type **2** and type **3** complexes. The results for the neopentylidene complexes are similar.

The ratio of type **3** to **2** depends on four variables. First, it depends on the solvent. For $Ta(CHPh)(PMe_3)_2Cl_3$ at −40 °C in $CDCl_3$ **3**/**2** = 3.5 but in CD_2Cl_2 **3**/**2** ≃ 0.5 while for $Ta(CHCMe_3)(PMe_3)_2Cl_3$ at −50 °C in $CHCl_3$ **3**/**2** ≃ 9 but in toluene **3**/**2** = 0.5. Second, it depends on the ligands. The ratio of **3** to **2** decreases as L is varied from PMe_3 to $PPhMe_2$ to PPh_2Me to THF or pyridine, and it increases on changing chloride to bromide (**3**/**2** = 7 for $Ta(CHPh)(PMe_3)_2Br_3$ in $CDCl_3$ at −40 °C; cf. 3.5 for $Ta(CHPh)(PMe_3)_2Cl_3$ above). Thirdly, the ratio of **3** to **2** increases as the temperature increases. Finally, the percentage of cis,*mer* is always larger when M = Nb than when M = Ta. Another important and curious fact is that the amount of **2** in $Ta(CHR)(PMe_3)_2Cl_3$ decreases when PMe_3 is added to the sample (Figure 2b).

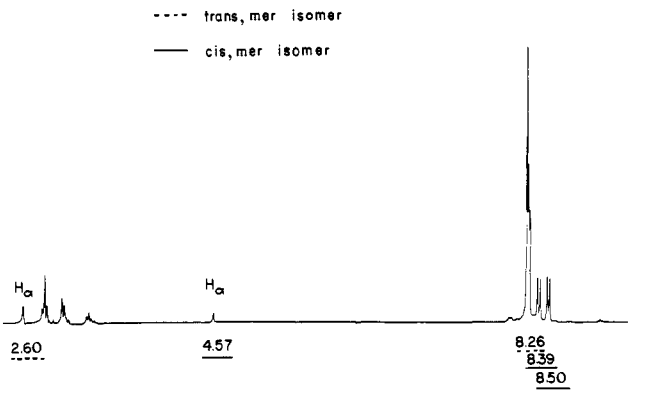
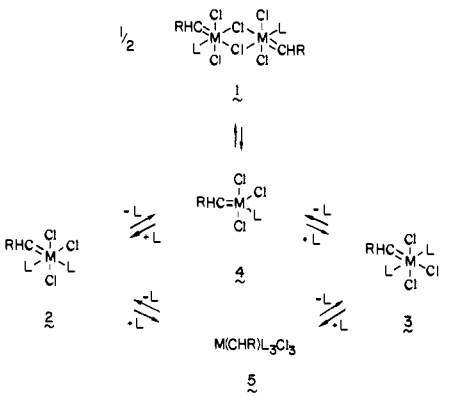


Figure 3. The 270-MHz ^1H NMR spectrum of $Ta(CHPh)(PMe_3)_2Cl_3$ in $CDCl_3$ at −40 °C (mixture of two isomers; see text).

Scheme I



All values for J_{CH_α} are low (70–100 Hz), as now expected for electron-deficient alkylidene complexes.[4,5] The low J_{CH_α} value in general has been ascribed to greater p character in the C_α–H_α bond due to a large M–C_α–R angle and interaction of M with the C–H_α electron pair.[5]

The ^1H NMR spectra of these octahedral neopentylidene and benzylidene complexes are all consistent with the proposed structures. For example, Figure 3 shows the 270-MHz ^1H NMR spectrum of $Ta(CHPh)(PMe_3)_2Cl_3$ (**3**/**2** mixture). The signal for the alkylidene H_α proton in all these complexes is found from ca. τ 2.5 to 6.5. Note that in several cases ligand exchange averages **2** and **3** at 30 °C so that only one average H_α is seen (see below).

One feature in the IR spectra of these complexes is important. The peak corresponding to the C–H_α stretching vibration is extraordinarily low and correlates roughly with J_{CH_α}. In $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$, ν_{CH_α} = 2605 cm^{-1} (J_{CH_α} = 101 Hz); in $Ta(CHCMe_3)(tmeda)Br_3$, ν_{CH_α} = 2400 cm^{-1} (J_{CH_α} = 70 Hz). We do not understand why ν_{CH_α} is comparatively weak in $Ta(CHPh)(PMe_3)_2X_3$ even though J_{CH_α} is low in each case (J_{CH_α} = 90 Hz when X = Cl; J_{CH_α} = 83 Hz when X = Br for type **3** isomers). The ν_{CH_α} stretch in other benzylidene complexes such as $Ta(\eta^5\text{-}C_5Me_5)(CHPh)Cl_2$[6] is also weak.

Interconversion of Alkylidene Complexes. The ^1H, ^{13}C, and ^{31}P NMR spectra of the $M(CHCMe_3)(L\text{–}L)X_3$ species are the same at −60 °C as at room temperature. Therefore, we know that L–L does not dissociate rapidly from M. However, in neither this nor any other case can we tell if the neopentylidene ligand begins to rotate rapidly on the NMR time scale (as found in the bis(cyclopentadienyl) class of compounds[7]).

The solution behavior of the $M(CHR)L_2X_3$ species is more complex. As the temperature of a typical sample is raised the

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(6) Messerle, L. W.; Jennische, P.; Schrock, R. R.; Stucky, G. *J. Am. Chem. Soc.*, in press.
(7) Schrock, R. R.; Messerle, L. W.; Wood, C. D.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1978**, *100*, 3793–3800.

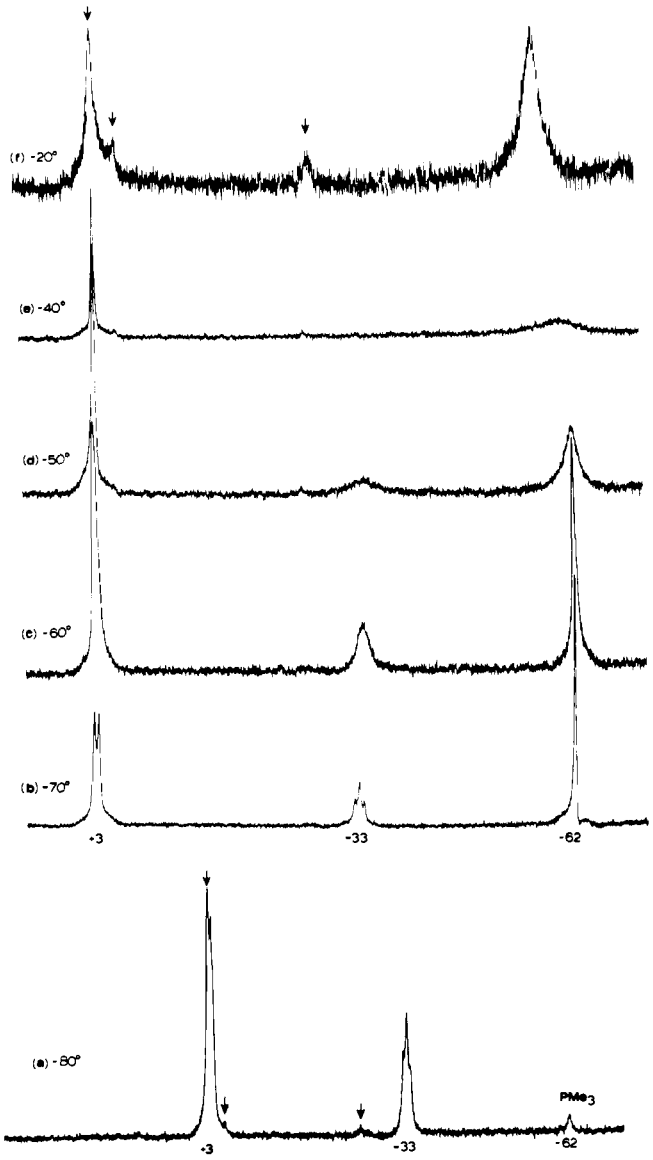
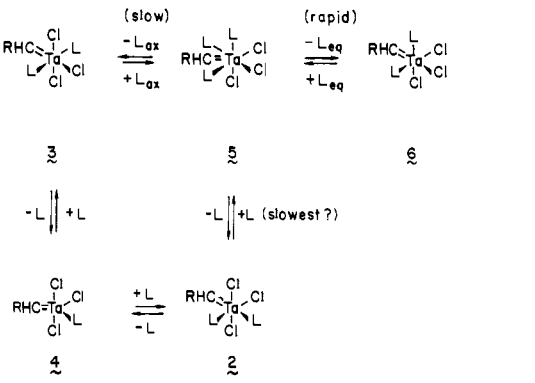


Figure 4. The temperature-dependent 36.43-MHz $^{31}P\{^1H\}$ NMR spectrum of $Ta(CHPh)(PMe_3)_3Cl_3$ in CH_2Cl_2: (a) in the presence of no excess PMe_3; (b)–(f) in the presence of 1 equiv of excess PMe_3. $J_{PP'}$ = 22 Hz in **5**; the three arrows mark the location of the signal for the PMe_3 ligands in **3** and the two signals for the PMe_3 ligands in **2**; note different scale in (a) vs. (b)–(f).

changes in the ^1H, ^{13}C, and ^{31}P NMR spectra suggest that the complex loses L and isomers **2** and **3** interconvert. A reasonable intermediate is a five-coordinate species, **4** (Scheme I). The proposed structure of **4** is arbitrary at this point, but the one shown in Scheme I is attractive since **2** is regenerated if L adds to **4** between RHC and L and **3** forms if L adds between RHC and equatorial Cl.

When excess L is added to $Ta(CHPh)(PMe_3)_2Cl_3$ in $CDCl_3$ and the sample cooled to −80 °C, the color changes from green to orange. The ^{31}P NMR spectrum shows that a seven-coordinate species (**5**) is present. It has two types of phosphine ligands with $J_{PP'}$ = 22 Hz. When little or no excess PMe_3 is present, **5** is in equilibrium with a small amount of **2** and **3** and PMe_3 (Figure 4a). Excess PMe_3 shifts the equilibrium toward **5** (Figure 4b). As the temperature of the sample is raised, more **2** and **3** form from **5** and the signals for **5** and free PMe_3 all broaden at about the same rate, while that due to **3** (which overlaps with one of those for **5**) remains relatively sharp (Figure 4e, compare also Figure 4d with Figure 2b). Figure 4f shows peaks for **2** and **3** (which finally begin to broaden due to exchange of phosphine) and a peak due to the average of free PMe_3 and the PMe_3 ligands in any **5** which remains at this temperature. The main point is

Scheme II



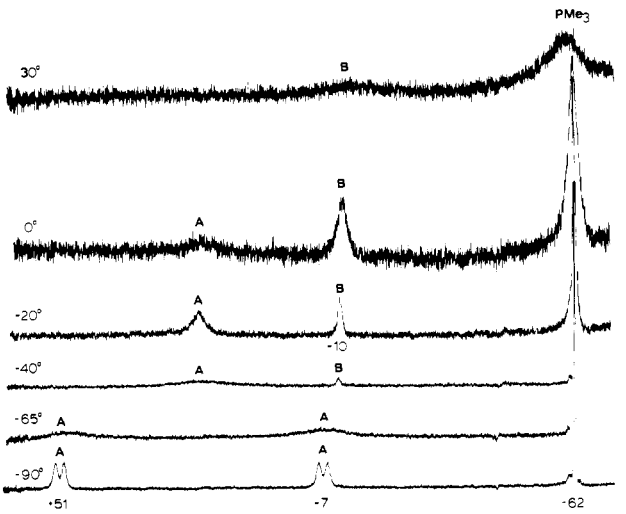


Figure 5. The variable-temperature 36.43-MHz $^{31}P\{^1H\}$ NMR spectrum of $Ta(CH_2Ph)_2Cl_3$ plus 4 equiv of PMe_3 in toluene: A = $Ta(CH_2Ph)_2(PMe_3)_2Cl_3$ ($J_{PP'}$ = 68 Hz); B = $Ta(CH_2Ph)_2(PMe_3)Cl_3$.

that free PMe_3 averages with bound PMe_3 in **5**, but *neither* ***2*** *nor* ***3*** *is part of this process*. An attractive possible explanation for this behavior is shown in Scheme II. If the structure of **5** is that shown, then loss of an equatorial L yields only **6**, the as yet unobserved third possible isomer. When the axial L is lost, **3** can be generated but this process should be more difficult. Interestingly, **2** should not form readily from **5** (or vice versa). It should form more readily via **4**. But exactly what are the relative rates of these various processes in any given situation should depend on R, L, M, temperature, and solvent. For example, the gross features of the neopentylidene system should be quite similar but the details (such as how low a temperature one must reach to see **5**) will almost certainly differ. In fact, we have not yet seen evidence for $Ta(CHCMe_3)(PMe_3)_3Cl_3$.

Formation of Alkylidene Complexes. We are now in a position to discuss how the alkylidene complexes form. Again, most data are for the benzylidene system. The experiment shown in Figure 5 consists of observing by $^{31}P\{^1H\}$ NMR at various temperatures a mixture of $Ta(CH_2Ph)_2Cl_3$ and ca. 4 equiv of PMe_3. At the lowest temperature we observe seven-coordinate $Ta(CH_2Ph)_2(PMe_3)_2Cl_3$ (**7**, R = Ph, eq 7). It contains nonequivalent PMe_3

$$Ta(CH_2R)_2(PMe_3)Cl_3 \underset{-L}{\overset{+L}{\rightleftharpoons}} \underset{\mathbf{7}}{Ta(CH_2R)_2(PMe_3)_2Cl_3} \quad (7)$$

ligands with $J_{PP'}$ = 68 Hz. As the sample is warmed slowly, $Ta(CH_2Ph)_2(PMe_3)_2Cl_3$ rearranges intramolecularly. Shortly thereafter it slowly loses PMe_3 to give $Ta(CH_2Ph)_2(PMe_3)Cl_3$ (**B**) and free PMe_3. Above −20 °C the phosphine ligands in $Ta(CH_2Ph)_2(PMe_3)Cl_3$ and $Ta(CH_2Ph)_2(PMe_3)_2Cl_3$ exchange with free phosphine at about the same rate. Cooling the sample back to −80 °C regenerates the spectrum of $Ta(CH_2Ph)_2(PMe_3)_2Cl_3$. These data establish that $Ta(CH_2Ph)_2(PMe_3)_2Cl_3$ is in equilibrium with $Ta(CH_2Ph)_2(PMe_3)Cl_3$. If the sample is now intermittently

warmed to 50 °C and examined at −80 °C, $Ta(CH_2Ph)_2(PMe_3)_2Cl_3$ disappears and **5** (Figure 4) and free PMe_3 appear. We have not yet seen $Ta(CH_2CMe_3)_2(PMe_3)_2Cl_3$ spectroscopically. We assume that it does form but loses PMe_3 much more easily than $Ta(CH_2Ph)_2(PMe_3)_2Cl_3$ due to the greater steric demand of the neopentyl ligand.

The $^{31}P\{^1H\}$ NMR spectrum of $Ta(CH_2CMe_3)_2(PMe_3)Cl_3$ in toluene at −90 °C shows a singlet at −16 ppm, but at −30 °C a second singlet appears at +29 ppm (~15% of the mixture) which we believe must be due to a second isomer of $Ta(CH_2CMe_3)_2(PMe_3)Cl_3$. At 0 °C both peaks broaden due to loss of PMe_3 from $Ta(CH_2CMe_3)_2(PMe_3)Cl_3$ and yield an average resonance which shifts toward the position where a peak for free PMe_3 would be found (average = −31 ppm at 40 °C; free PMe_3 = −62 ppm). By this time the mixture contains mostly *trans,mer*-$Ta(CHCMe_3)(PMe_3)_2Cl_3$ and *cis,mer*-$Ta(CHCMe_3)(PMe_3)_2Cl_3$. This behavior contrasts sharply with that for $Ta(CH_2Ph)_2(PMe_3)Cl_3$. In the $^{31}P\{^1H\}$ NMR spectrum at 50 °C the signal for $Ta(CH_2Ph)_2(PMe_3)Cl_3$ is still sharp and only slightly upfield of its position (~40 ppm below PMe_3) in a spectrum at 0 °C. Therefore, the equilibrium between $Ta(CH_2Ph)_2(PMe_3)Cl_3$, $Ta(CH_2Ph)_2Cl_3$, and PMe_3 lies well toward $Ta(CH_2Ph)_2(PMe_3)Cl_3$ at 50 °C. As we stated earlier, $Ta(CH_2Ph)_2(PMe_3)Cl_3$ decomposes little in 1 h at 50 °C, a temperature where α abstraction in the presence of excess PMe_3 is comparatively rapid.

Low-temperature ^{13}C NMR spectra of $Ta(CH_2R)_2(PMe_3)Cl_3$ show one signal for the CH_2R α-carbon atoms while the ^1H NMR spectra show only one signal for the CH_2R α protons at 270 MHz. These data are most consistent with a trans,*mer* structure. We were not able to obtain any information concerning the structure of the minor isomer of $Ta(CH_2CMe_3)_2(PMe_3)Cl_3$ which we observed in the low-temperature $^{31}P\{^1H\}$ NMR spectrum.

A plausible structure for $Ta(CH_2Ph)_2(PMe_3)_2Cl_3$ is a pentagonal bipyramid containing one axial and one equatorial PMe_3 ligand.

Decomposition of Alkylidene Complexes. When a sample of $Ta(CHPh)(PMe_3)_2Cl_3$ is heated in benzene for 21 h at 60 °C, it decomposes to give a mixture of toluene and *cis*- and *trans*-stilbene (eq 8). $Ta(CHCMe_3)(PMe_3)_2Cl_3$ is much more stable;

$$Ta(CHPh)(PMe_3)_2Cl_3 \xrightarrow[60\ °C,\ 21\ h]{\text{benzene}} \underset{14\%}{\text{toluene}} + \underset{10\%}{\textit{cis}\text{-stilbene}} + \underset{30\%}{\textit{trans}\text{-stilbene}} \quad (8)$$

after 24 h at 130 °C in toluene, it decomposes only partially to give mostly neopentane and some *trans*-2,2,5,5-tetramethyl-3-hexene (eq 9). These decompositions are slowed by adding PMe_3.

$$Ta(CHCMe_3)(PMe_3)_2Cl_3 \xrightarrow[100\ °C,\ 24\ h]{\text{benzene}} \underset{40\%}{CMe_4} + \underset{3\%}{\textit{trans}\text{-}Me_3CCH{=}CHCMe_3} \quad (9)$$

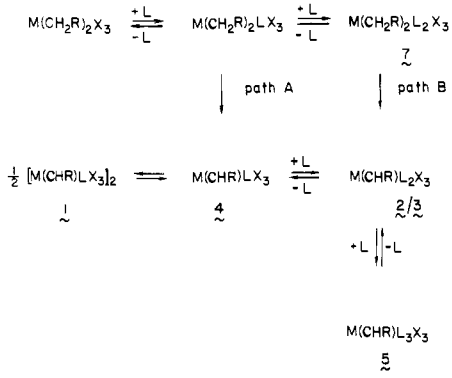
Therefore, loss of PMe_3 from the six-coordinate species seems to be the first step in a decomposition reaction. It seems quite reasonable on the basis of previous studies[8] that the olefins form in a bimolecular reaction, most likely involving five-coordinate **4** (Scheme I). Since dimeric **1** has not yet been observed when R = Ph, we believe that two benzylidene ligands can couple much more readily than two neopentylidene ligands, probably largely for steric reasons. One role of the excess PMe_3 in the formation of $Ta(CHPh)(PMe_3)_2Cl_3$, therefore, is to prevent decomposition, mostly by preventing formation of $Ta(CHPh)(PMe_3)Cl_3$.

Based on the above findings, we can now understand why neopentylidene complexes containing bidentate ligands are much more stable than those containing monodentate ligands. $Ta(CHCMe_3)(bpy)Cl_3$ can even be sublimed unchanged.

Discussion

The simplest hypothesis as to how these octahedral alkylidene complexes form is that α abstraction is most rapid in a seven-coordinate complex (path B in Scheme III), either the one we have observed at low temperature or another which is available by ready intramolecular rearrangement. This hypothesis rests on the observation that $Ta(CH_2Ph)_2(PMe_3)Cl_3$ is stable at 50 °C, apparently because it does not lose PMe_3 to any significant extent. Therefore, path A is slow for *this* six-coordinate species. In contrast, $Ta(CH_2CMe_3)_2(PMe_3)Cl_3$ does lose PMe_3 readily so that **7** and eventually 0.5 equiv of **2/3** can form; **2/3** then yields **1** plus free PMe_3 which attacks more $Ta(CH_2CMe_3)_2Cl_3$ to give **7**, etc., until all $Ta(CH_2CMe_3)_2(PMe_3)Cl_3$ is converted to **1** and neopentane. The seven-coordinate hypothesis is also consistent with the fact that the α-abstraction reaction is faster with smaller, more basic phosphines.

Scheme III



There is at least one reasonable alternative to the seven-coordinate hypothesis; an unobservable six-coordinate complex is the immediate precursor to the alkylidene complex, but it is accessible only via a seven-coordinate species. (We should point out that α-abstraction probably does occur in some six-coordinate neopentyl complexes.[4]) A further complication might be that the immediate precursor to a neopentylidene complex is six-coordinate while that to a benzylidene complex is seven-coordinate.

We have no reason to suspect that the requirements for α abstraction in this system differ substantially from those for α abstraction in the $Ta(\eta^5\text{-}C_5R_5)(CH_2CMe_3)_2X_2$ system.[3] In particular, the two alkyl groups in the immediate precursor to an alkylidene complex almost certainly must be close to one another (C–M–C ≈ 90° or less), and the molecule must be crowded. In the $Ta(\eta^5\text{-}C_5R_5)(CH_2CMe_3)_2X_2$ system the effect of X and solvent was similar to that observed here and could be explained partially, but not completely, in terms of the required cis geometry. But we have no way of knowing here whether X = Br and polar S similarly increase the likelihood of a cis (or pseudo-cis) geometry in the immediate precursor to the alkylidene complex or whether more subtle effects are also important.

Since the details of the α-abstraction reactions are not known, we have no hard evidence concerning the relative rates of α abstraction in neopentyl vs. benzyl or trimethylsilylmethyl complexes. However, qualitatively we feel that neopentyl complexes are inherently more prone to α abstraction than benzyl or trimethylsilylmethyl complexes, and these in turn are more prone to α abstraction than methyl complexes. In fact, seven-coordinate methyl complexes such as $TaMe_2(PMe_3)_2Br_3$ are quite stable thermally.[9] An attempt to force the α-abstraction reaction by using a more bulky mesityl ligand as the leaving group in $TaMeMes(PMe_3)_2Br_3$ gave a substituted benzylidene complex by γ abstraction of a hydrogen atom followed by rearrangement of the postulated intermediate benzotantallacyclobutene complex.[10] So far we still have no route to what we expect to be isolable methylene complexes, $M(CH_2)L_2X_3$.

There is now little doubt that an alkylidene ligand will donate electron density from its CH_α bond to a sufficiently electron deficient metal, just as oxo[11] and imido[12] ligands donate (almost

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(9) Sharp, P. R., unpublished results.

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certainly more easily) a lone pair of electrons. This results in low values for J_{CH_α} and ν_{CH_α}. Judging from the neutron diffraction study on $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$,[5] H_α probably comes close to occupying a coordination position in the more extreme cases. As a result, these molecules almost certainly will be distorted toward a "pentagonal-bipyramidal" geometry. This could in turn help explain why monodentate L is so labile in these complexes, and therefore why all such alkylidene complexes (except when chelating ligands are present) interconvert so readily.

Experimental Section

All experiments were done under nitrogen either by standard Schlenk techniques or in a Vacuum Atmospheres HE 43-2 drybox. Solvents were rigorously purified and dried under N_2 by standard techniques and transferred into the drybox without exposure to air. $Ta(CH_2CMe_3)_2X_3$ (X = Cl, Br),[3] $Nb(CH_2CMe_3)_2Cl_3$,[3] $Ta(CH_2Ph)_2Cl_3$,[6] PMe_3,[13] and dmpe[14] were prepared by published methods. Metal halides were purchased from standard sources. Bulk liquids were dried and distilled in a recommended manner. TlC_5H_5 was purchased and sublimed before use. TlC_5Me_5 was prepared from Tl_2SO_4 and LiC_5Me_5 (see preparation 33).

NMR spectra were run at ca. 35 °C and 60 MHz (^1H), 15 or 22.63 MHz (^{13}C), or 36.43 MHz (^{31}P) unless otherwise noted. ^{13}C spectra are reported in the ^1H-gated decoupled mode (unless otherwise noted). If coupling to phosphorus can be observed in the ^1H decoupled spectrum, then it is reported as part of the data for the ^1H gated decoupled spectrum even though in this mode long-range C–H coupling usually obscures small CP couplings. Note that at room temperature cis,*mer* and trans,*mer* isomers normally are interconverting at a rate on the order of the NMR time scale by loss of L so that an average spectrum is obtained and any C–P coupling is lost. GLC samples were analyzed with an HP 5730A chromatograph and 3380A recorder on an 8-ft 10% SP-2100 on Supelcoport or a 15-ft 10% SE-30 on 100/120 Gas Chrom Q column. Molecular weights were determined by freezing-point depression under N_2 in cyclohexane or benzene.

We believe that the lability of monodentate ligands in complexes of the type $M(CHR)L_2X_3$ is what has consistently led to unacceptably low C and H analytical results despite numerous attempts and procedural variations. Compounds in which ligands are not especially labile ($[Ta(CHCMe_3)(PMe_3)Cl_3]_2$, $Ta(CHCMe_3)(tmeda)Cl_3$, etc.) analyzed satisfactorily. Yields are greater than 90% unless otherwise stated.

Preparations. (1) $Ta(CH_2CMe_3)_2(PMe_3)Cl_3$. PMe_3 (0.36 g) in 2 mL of pentane was added dropwise with stirring to $Ta(CH_2CMe_3)_2Cl_3$ (2.15 g) in 15 mL of pentane at −30 °C. The yellow solution became red as the PMe_3 was added, and orange-red needles were precipitated. After 2 min, the product was collected by filtration, rinsed with cold pentane, and dried briefly in vacuo. $Ta(CH_2CMe_3)_2(PMe_3)Cl_3$ is thermally unstable and must be stored at −30 °C. It can be recrystallized from a saturated ether solution at −30 °C.

^1H NMR ($C_6D_6CD_3$, −80 °C, 270 MHz): τ 7.65 (d, 4, $^3J_{HP}$ = 12.0 Hz, CH_2CMe_3), 8.46 (s, 18, CH_2CMe_3), 9.37 (d, 9, $^2J_{HP}$ = 8.4 Hz, PMe_3). ^{13}C NMR ($C_6D_5CD_3$, −60 °C, 67.89 MHz): 96.1 (t, J_{CH} = 121 Hz, CH_2CMe_3), 45.6 (s, CH_2CMe_3), 35.1 (q, J_{CH} = 124 Hz, CH_2CMe_3), 12.1 ppm (qd, J_{CH} = 131 Hz, J_{CP} = 21 Hz, PMe_3). $^{31}P\{^1H\}$ NMR (toluene, −50 °C, 36.43 MHz): −16.4 ppm (s).

(2) $Ta(CHCMe_3)(PMe_3)_2Cl_3$. PMe_3 (4.68 g) in 10 mL of pentane was added dropwise with stirring to $Ta(CH_2CMe_3)_2Cl_3$ (12.90 g) in 60 mL of pentane at −30 °C. The yellow solution became red, and needles of $Ta(CH_2CMe_3)_2(PMe_3)Cl_3$ precipitated. In ca. 30 min, these dissolved to give a dark red solution which became purple after the reaction was warmed to 25 °C. After 3 h the pentane was removed in vacuo to give a purple oil which slowly precipitated from a saturated 9:1 ether/pentane solution as a purple-pink powder. It can be recrystallized from ether at −30 °C in the form of fibers.

$Ta(CHCMe_3)(PMe_3)_2Cl_3$ can also be prepared quantitatively by adding 1 equiv of PMe_3 to $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$ in toluene or ether.

^1H NMR ($C_6D_5CD_3$, −60 °C, 270 MHz): for the cis,*mer* isomer, τ 6.03 (br s, 1, $CHCMe_3$), 8.78 (d, 9, $^2J_{HP}$ = 8.7 Hz, PMe_3), 8.87 (s, $CHCMe_3$), 8.96 (d, 9, $^2J_{HP}$ = 6.9 Hz, PMe_3'); for the trans,*mer* isomer, τ 3.91 (br s, 1, $CHCMe_3$), 8.70 (t, 18, $^2J_{HP} \approx 4$ Hz, PMe_3), 8.82 (s, 9, $CHCMe_3$). ^{13}C NMR ($C_6D_5CD_3$, −50 °C, 67.89 MHz): for the cis,*mer* isomer, 255.9 (ddd, J_{CH} = 96 Hz, $^2J_{CP'}$ = 33 Hz, $^2J_{CP}$ = 12 Hz, $CHCMe_3$), 46.8 (d, $^3J_{CP'}$ = 13 Hz, $CHCMe_3$), 33.2 (q, J_{CH} = 127 Hz, $CHCMe_3$), 18.0 (qd, J_{CH} = 129 Hz, J_{CP} = 28 Hz, PMe_3), 12.3 ppm (qd, J_{CH} = 132 Hz, $J_{CP'}$ = 16 Hz, PMe_3'); for the trans,*mer* isomer, 256.5 (dt, J_{CH} = 75 Hz, $^2J_{CP}$ = 12 Hz, $CHCMe_3$), 45.8 (s, $CHCMe_3$), 34.5 (q, J_{CH} = 125 Hz, $CHCMe_3$), 155 ppm (qt, J_{CH} = 134 Hz, J_{CP} = 15 Hz, PMe_3). $^{31}P\{^1H\}$ NMR (toluene, −70 °C, 36.43 MHz): for the cis,*mer* isomer, −5.7 (d, $^2J_{PP'}$ = 7 Hz), −20.5 ppm (d, $^2J_{P'P}$ = 7 Hz); for the trans,*mer* isomer, −4.9 ppm (s). IR (Nujol/NaCl): 2510 (m, ν_{CH_α}) cm^{-1}. M_r (C_6H_6, 6.36 mM): calcd 510; found 377.

(3) $Ta(CHCMe_3)(PPhMe_2)_2Cl_3$. $PPhMe_2$ (0.84 g) in 10 mL of pentane was added dropwise with stirring to $Ta(CH_2CMe_3)_2Cl_3$ (1.29 g) in 20 mL of pentane at −30 °C. The yellow solution became red. After 1–2 h at 25 °C a red-purple microcrystalline solid formed. This crude product was recrystallized from toluene/pentane at −30 °C.

^1H NMR (C_6D_6): τ 2.45–3.05 (m, 10, Ph), 8.48 (br, 12, $PPhMe_2$), 8.89 (s, 9, $CHCMe_3$). ^1H NMR ($C_6D_5CD_3$, −50 °C, 270 MHz): for the cis,*mer* isomer, τ 2.50–3.05 (m, 10, Ph), 5.95 (s, 1, $CHCMe_3$), 8.65 (d, 6, $^2J_{HP}$ = 8.4 Hz, $PPhMe_2$), 8.80 (d, 6, $^2J_{HP'}$ = 5.8 Hz, $PPhMe_2$), 8.88 (s, 9, $CHCMe_3$); for the trans,*mer* isomer, τ 2.50–3.05 (m, 10, Ph), 3.94 (s, 1, $CHCMe_3$), 8.31 (t, 6, $^2J_{HP}$ = 3.9 Hz, $PPhMeMe'$), 8.84 (t, 6, $^2J_{HP}$ = 3.9 Hz, $PPhMeMe'$), 9.29 (s, 9, $CHCMe_3$). ^{13}C NMR (C_6D_6, average of isomers): 262 (br d, J_{CH} = 88 Hz, $CHCMe_3$), 137.0 (s, C_{ipso}), 130.9 (d, J_{CH} = 162 Hz, C_{ortho}), 129.9 (d, J_{CH} = 162 Hz, C_{para}), 128.6 (d, J_{CH} = 160 Hz, C_{meta}), 46.8 (s, $CHCMe_3$), 33.2 (q, J_{CH} = 127 Hz, $CHCMe_3$), 17.1 (qd, J_{CH} = 131 Hz, J_{CP} = 20 Hz, $PPhMe_2$), 11.1 ppm (qd, J_{CH} = 132 Hz, J_{CP} = 18 Hz, $PPhMe_2$). $^{31}P\{^1H\}$ NMR (toluene, −50 °C, 36.43 MHz): for the cis,*mer* isomer, −0.8 (br s), −25.7 ppm (br s); for the trans,*mer* isomer, 1.8 ppm (s). IR (Nujol/NaCl): 2520 (m, ν_{CH_α}) cm^{-1}.

(4) $Ta(CHCMe_3)(PPh_2Me)_2Cl_3$. A procedure analogous to the above employing 1.20 g of PPh_2Me gave 2.09 g (92%) of $Ta(CHCMe_3)(PPh_2Me)Cl_3$.

^1H NMR (C_6D_6): τ 2.35–3.10 (m, 20, Ph), 4.50 (s, 1, $CHCMe_3$), 8.34 (br, 6, PPh_2Me), 8.87 (s, 9, $CHCMe_3$). IR (Nujol/NaCl): 2535 (vw, ν_{CH_α}) cm^{-1}.

(5) $Ta(CHCMe_3)(PMe_3)_2Br_3$. PMe_3 (0.80 g) in 2 mL of pentane was added dropwise with stirring to $Ta(CH_2CMe_3)_2Br_3$ (2.82 g) in 15 mL of pentane at −30 °C. The yellow solution became dark red immediately and purple needles (presumably $Ta(CH_2CMe_3)_2(PMe_3)Br_3$) precipitated. These dissolved rapidly to give a blue-purple solution in which blue-purple crystals formed. The product was collected by filtration, rinsed with pentane, and dried in vacuo.

^1H NMR (C_6D_6): τ 8.54 (br, 18, PMe_3), 8.67 (s, 9, $CHCMe_3$). ^{13}C NMR ($CDCl_3$, −20 °C, 15 MHz): for the trans,*mer* isomer, 258.7 (dt, J_{CH} = 74 Hz, $^2J_{CP}$ = 8 Hz, $CHCMe_3$), 45.6 (s, $CHCMe_3$), 33.2 (q, J_{CH} = 125 Hz, $CHCMe_3$), 16.5 ppm (qt, J_{CH} = 132 Hz, J_{CP} = 15 Hz, PMe_3). $^{31}P\{^1H\}$ NMR (toluene, −50 °C, 36.43 MHz): for the cis,*mer* isomer, −9.2 (br s), −31.1 ppm (br s); for the trans,*mer* isomer, −4.0 ppm (s). IR (Nujol/NaCl): 2505 (m, ν_{CH_α}) cm^{-1}.

(6) $Nb(CHCMe_3)(PMe_3)_2Cl_3$. PMe_3 (1.44 g) in 3 mL of pentane was added dropwise with stirring to $Nb(CH_2CMe_3)_2Cl_3$ (3.08 g) in 50 mL of pentane at −30 °C. Red-brown crystals (probably $Nb(CH_2CMe_3)_2(PMe_3)Cl_3$) formed initially but dissolved rapidly to give a purple solution and a green-brown precipitate. The solution was filtered immediately and the pentane removed in vacuo, leaving a blue-purple powder, yield 2.5 g (66%). Larger scale reactions gave lower yields.

^1H NMR (C_6H_6): τ 5.43 (br, 1, $CHCMe_3$), 8.75 (br, 18, PMe_3), 8.83 (s, 9, $CHCMe_3$). ^1H NMR ($CDCl_3$, −30 °C, 60 MHz): for the cis,*mer* isomer, τ 5.84 (d, $^3J_{HP}$ = 6.5 Hz, $CHCMe_3$), 8.31–8.54 (m, 18, PMe_3 and PMe_3'), 8.71 (s, 9, $CHCMe_3$); for the trans,*mer* isomer, τ 4.37 (br, 1, $CHCMe_3$), 8.71 (s, 9, $CHCMe_3$), 8.50 (t, $J_{HP} \approx 4$ Hz, PMe_3). ^{13}C NMR ($CDCl_3$, −30 °C, 15 MHz): for the cis,*mer* isomer, 252.8* (br d, J_{CH} = 79 Hz, $CHCMe_3$), 45.9 (s, $CHCMe_3$), 29.2 (q, J_{CH} = 126 Hz, $CHCMe_3$), 16.6 (qd, J_{CH} = 137 Hz, J_{CP} = 25 Hz, PMe_3), 11.6 ppm (qd, J_{CH} = 137 Hz, J_{CP} = 16 Hz, PMe_3); for the trans,*mer* isomer, 252.8* (br d, J_{CH} = 79 Hz, $CHCMe_3$), 46.5 (s, $CHCMe_3$), 29.8 (q, J_{CH} = 126 Hz, $CHCMe_3$), 14.2 (qt, J_{CH} = 137 Hz, J_{CP} = 13 Hz, PMe_3). $^{31}P\{^1H\}$ NMR (toluene, −50 °C, 36.43 MHz): for the cis,*mer* isomer, −10.9 (br s), −26.9 ppm (br s); for the trans,*mer* isomer, −10.0 ppm (s). IR (Nujol/NaCl): 2510 (br m, ν_{CH_α}) cm^{-1}. The asterisk indicates coincidence of two C_α resonances.

(7) $Nb(CHCMe_3)(PPhMe_2)_2Cl_3$. $PPhMe_2$ (1.66 g) in 5 mL of pentane was added dropwise with stirring to $Nb(CH_2CMe_3)_2Cl_3$ (2.05 g) in 50 mL of pentane at −30 °C. After the reaction had warmed to 25 °C, a purple suspension formed and a brown tar was deposited on the bottom

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(16) Threlkel, R. S.; Bercaw, J. E. *J. Organomet. Chem.* **1977**, *136*, 1–5.

of the reaction flask. The purple suspension was decanted from the tar and filtered. The purple powder was dissolved in toluene and crystallized at −30 °C by adding pentane; yield 2.01 g (61%).

^{1}H NMR (C_6D_6): τ 2.40–3.00 (m, 10, Ph), 5.45 (br s, 1, C*H*CMe$_3$), 8.61 (br, 12, PPh*Me*$_2$), 8.95 (s, 9, CHC*Me*$_3$).

(8) Ta(CHCMe$_3$)(dmpe)Cl$_3$. Dmpe (0.75 g) in 3 mL of $CHCl_3$ was added dropwise with stirring to Ta(CH$_2$CMe$_3$)$_2$Cl$_3$ (2.15 g) in 20 mL of $CHCl_3$ at −30 °C. At 25 °C the yellow solution slowly turned deep red. After 8 h the reaction mixture was filtered and the solvent removed from the filtrate in vacuo to yield a red solid which was recrystallized from toluene (15 mL) at −30 °C by adding pentane (2–5 mL); yield 2.24 g (88%).

^{1}H NMR (C_6D_6): τ 6.20 (dd, 1, $^3J_{HP'}$ = 5.2 Hz, $^3J_{HP}$ = 1.0 Hz, C*H*CMe$_3$), 8.30–8.90 (m, 4, Me$_2$PC*H*$_2$C*H*$_2$P'Me$_2$), 8.61 (d, 6, $^2J_{HP}$ = 9.4 Hz, −P*Me*$_2$), 8.81 (d, 6, $^2J_{HP'}$ = 8.0 Hz, −P'*Me*$_2$), 8.84 (s, 9, CHC*Me*$_3$). ^{13}C NMR ($CDCl_3$): 243.0 (ddd, J_{CH} = 72 Hz, $^2J_{CP'}$ = 23 Hz, $^2J_{CP}$ = 13 Hz, *C*HCMe$_3$), 46.0 (d, $^3J_{CP'}$ = 13 Hz, CH*C*Me$_3$), 33.5 (q, J_{CH} = 126 Hz, CHC*Me*$_3$), 27.5 (m, J_{CP} = 26 Hz, $^2J_{CP'}$ = 13 Hz, −*C*H$_2$PMe$_2$), 24.0 (m, $J_{CP'}$ = 20 Hz, $^2J_{CP}$ = 8 Hz, −*C*H$_2$P'Me$_2$), 15.0 (qd, J_{CH} = 132 Hz, J_{CP} = 32 Hz, −P*Me*$_2$), 9.0 ppm (qd, J_{CH} = 132 Hz, $J_{CP'}$ = 19 Hz, −P'*Me*$_2$). ^{31}P{^{1}H} NMR ($CHCl_3$, −50 °C, 36.43 MHz): 20.5 (br s), 0.6 ppm (br s).

(9) [Ta(CHCMe$_3$)(dmpe)Cl$_3$]$_x$. (a) From Ta(CH$_2$CMe$_3$)$_2$Cl$_3$. Dmpe (0.30 g) in 2 mL of pentane was added dropwise with stirring to Ta(CH$_2$CMe$_3$)$_2$Cl$_3$ (0.86 g) in 10 mL on pentane at −30 °C. The yellow solution became colorless as a white microcrystalline solid precipitated over a 12-h period.

(b) From Ta(CHCMe$_3$)(PMe$_3$)$_2$Cl$_3$. Dmpe (0.08 g) in 1 mL of ether was added dropwise with stirring to Ta(CHCMe$_3$)(PMe$_3$)$_2$Cl$_3$ (0.25 g) in 4 mL of ether. The purple solution became colorless as the polymer precipitated quantitatively (0.25 g).

(c) From Ta(CHCMe$_3$)(dmpe)Cl$_3$. An ether solution of Ta(CHCMe$_3$)(dmpe)Cl$_3$ (0.25 g) at 25 °C deposited a white powder quantitatively (0.25 g) over a 3-day period.

IR (Nujol/NaCl): 2498 (w, ν_{CH_a}) cm^{-1}.

A suspension of 75 mg of [Ta(CHCMe$_3$)(dmpe)Cl$_3$]$_x$ in 5 mL of mesitylene (plus octane as internal standard) was stirred at 100 °C for 1 day under 50 psi of ethylene in a pressure bottle. An aliquot was shown to contain (by GLC) 0.31 equiv of 4,4-dimethyl-1-pentene and 0.56 equiv of *trans*-4,4-dimethyl-2-pentene, typical products of a reaction between an alkylidene complex and an olefin.[4,15]

(10) Ta(CHCMe$_3$)(tmeda)Cl$_3$. Tmeda (0.58 g) in 5 mL of CH_2Cl_2 was added dropwise with stirring to Ta(CH$_2$CMe$_3$)$_2$Cl$_3$ (2.15 g) in 20 mL of CH_2Cl_2 at −30 °C. The yellow solution immediately became purple. After 2 h at 25 °C the solvent was removed in vacuo to give a purple solid which was recrystallized from a saturated Et_2O solution at −30 °C by adding pentane.

Anal. Calcd for $TaC_{11}H_{26}N_2Cl_3$: C, 27.90; H, 5.53; N, 5.91. Found: C, 27.92; H, 5.71; N, 5.72. M_r (cyclohexane, 13.55 mM): calcd 474; found 489. ^{1}H NMR ($CDCl_3$): τ 6.45 (s, 1, C*H*CMe$_3$), 6.82 (s, 6, −NMe$_2$), 6.99 (m, 2, −C*H*$_2$NMe$_2$), 7.20 (m, 2, −C*H*$_2$N'Me$_2$), 7.29 (s, 6, −N'*Me*$_2$), 8.84 (s, 9, CHC*Me*$_3$). ^{13}C NMR ($CDCl_3$): 248.4 (d, J_{CH} = 79 Hz, *C*HCMe$_3$), 60.3 (t, J_{CH} = 138 Hz, −*C*H$_2$NMe$_2$), 57.6 (t, J_{CH} = 135 Hz, −*C*H$_2$N'Me$_2$), 56.6 (q, J_{CH} = 139 Hz, − NMe$_2$), 49.6 (q, J_{CH} = 138 Hz, −N'*Me*$_2$), 45.8 (s, CHCMe$_3$), 33.6 ppm (q, J_{CH} = 126 Hz, CHC*Me*$_3$). IR (Nujol/NaCl): 2532 (m, ν_{CH_a}) cm^{-1}.

(11) Ta(CHCMe$_3$)(bpy)Cl$_3$. A solution of bpy (0.78 g) in 10 mL of CH_2Cl_2 was added dropwise with stirring to Ta(CH$_2$CMe$_3$)$_2$Cl$_3$ (2.15 g) in 20 mL of CH_2Cl_2 at −30 °C. The yellow solution immediately turned dark blue-purple, and blue-purple crystals formed as the solution warmed to 25 °C. A second crop was obtained by reducing to volume of the mother liquor in vacuo and cooling to −30 °C for 2 h.

Anal. Calcd for $TaC_{15}H_{18}N_2Cl_3$: C, 35.08; H, 3.53; N, 5.46. Found: C, 35.11; H, 3.63; N, 5.60. ^{1}H NMR (CH_2Cl_2): τ 0.10–2.50 (m, 8, bpy), 6.67 (s, 1, C*H*CMe$_3$), 8.68 (s, 9, CHC*Me*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): 247.1 (s, *C*HCMe$_3$), 158.6, 157.0, 151.2, 149.9, 141.1, 140.2, 128.2, 127.0, 122.9, 122.9 (all s, bpy), 46.42 (s, CH*C*Me$_3$), 33.7 ppm (s, CHC*Me*$_3$).

(12) Ta(CHCMe$_3$)(diars)Cl$_3$. Diars (0.86 g) in 1 mL of CH_2Cl_2 was added dropwise with stirring to Ta(CH$_2$CMe$_3$)$_2$Cl$_3$ (1.29 g) in 10 mL of CH_2Cl_2 at −30 °C. After 8 h at 25 °C the solvent was removed in vacuo. The crude product was recrystallized from a saturated toluene solution by adding pentane until the solution became cloudy and cooling to −30 °C.

^{1}H NMR ($CDCl_3$): τ 2.47 (m, 4, C_6H_4), 6.52 (s, 1, C*H*CMe$_3$), 8.54 (s, 6, −AsMe$_2$), 8.73 (s, 6, −As'*Me*$_2$), 8.77 (s, 9, CHC*Me*$_3$). ^{13}C NMR ($CDCl_3$): 247.4 (d, J_{CH} = 73 Hz, *C*HCMe$_3$), 142.6 (s), 141.4 (s), 132.3 (d, J_{CH} = 161 Hz), and 131.6 (d, J_{CH} = 161 Hz) (all due to C_6H_4 carbons), 46.3 (s, CH*C*Me$_3$), 33.5 (q, J_{CH} = 126 Hz, CHC*Me*$_3$), 14.9 (q, J_{CH} = 136 Hz, −As*Me*$_2$), 8.9 ppm (q, J_{CH} = 136 Hz, −As'*Me*$_2$). IR (Nujol/NaCl): 2490 (m, ν_{CH_a}) cm^{-1}.

(13) Ta(CHCMe$_3$)(dmpe)Br$_3$. Dmpe (0.61 g) in 2 mL of CH_2Cl_2 was added dropwise with stirring to Ta(CH$_2$CMe$_3$)$_2$Br$_3$ (2.25 g) in 10 mL of CH_2Cl_2 at −30 °C. After 8 h at 25 °C the solvent was removed in vacuo and the crude product recrystallized from toluene at −30 °C by adding pentane to give blue-purple crystals.

Anal. Calcd for $TaC_{11}H_{26}Br_3P_2$: C, 20.62; H, 4.09. Found: C, 21.02; H, 4.24. M_r (C_6H_6, 6.12 mM): calcd 641; found 653. ^{1}H NMR ($CDCl_3$): τ 6.65 (dd, 1, $^3J_{HP'}$ = 9.6 Hz, $^3J_{HP}$ = 1.3 Hz, C*H*CMe$_3$), 7.97–8.17 (m, 4, C_2H_4), 8.25 (d, 6, $^2J_{HP}$ = 9.5 Hz, −PMe$_2$), 8.36 (d, 6, $^2J_{HP'}$ = 8.6 Hz, −P'Me$_2$), 8.74 (s, 9, CHC*Me*$_3$). ^{13}C NMR ($CDCl_3$): 248.3 (ddd, J_{CH} = 72 Hz, $^2J_{CP'}$ = 16 Hz, $^2J_{CP}$ = 13 Hz, *C*HCMe$_3$), 46.5 (s, CH*C*Me$_3$), 33.4 (q, J_{CH} = 125 Hz, CHC*Me*$_3$), 28.0 (m, J_{CP} = 27 Hz, $^2J_{CP'}$ = 13 Hz, −*C*H$_2$PMe$_2$), 24.3 (m, $J_{CP'}$ = 21 Hz, $^2J_{CP}$ = 8 Hz, −*C*H$_2$P'Me$_2$), 19.1 (qd, J_{CH} = 126 Hz, J_{CP} = 31 Hz, −PMe$_2$), 10.6 ppm (qd, J_{CH} = 130 Hz, $J_{CP'}$ = 19 Hz, −P'Me$_2$). ^{31}P{^{1}H} NMR (toluene, −30 °C, 36.43 MHz): 13.7 (d, $J_{PP'}$ = 18 Hz), −3.1 ppm (d, $J_{P'P}$ = 18 Hz). IR (Nujol/NaCl): 2427 (m, ν_{CH_a}) cm^{-1}.

(14) Ta(CHCMe$_3$)(diphos)Br$_3$. A solution of diphos (1.59 g) in 5 mL of CH_2Cl_2 was added dropwise with stirring to Ta(CH$_2$CMe$_3$)$_2$Br$_3$ (2.25 g) in 10 mL of CH_2Cl_2 at −30 °C. After 8 h the solvent was removed in vacuo and the product was recrystallized from ether at −30 °C by adding pentane to give green crystals.

^{1}H NMR ($CDCl_3$): τ 1.87–2.93 (m, 20, Ph), 6.35 (s, 1, C*H*CMe$_3$), 6.74–6.95 (m, 4, PC$_2$H$_4$P), 8.57 (s, 9, CHC*Me*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): 263.1 (dd, $^2J_{CP'}$ = 28 Hz, $^2J_{CP}$ = 10 Hz, *C*HCMe$_3$), 137.5–125.1 (m, Ph), 48.2 (d, $^3J_{CP'}$ = 12 Hz, CH*C*Me$_3$), 32.9 (s, CHC*Me*$_3$), 23.0 (dd, J_{CP} = 24 Hz, $^2J_{CP'}$ = 12 Hz, −*C*H$_2$PPh$_2$), 20.7 ppm (dd, $J_{CP'}$ = 18 Hz, $^2J_{CP}$ = 9 Hz, −*C*H$_2$P'Ph$_2$).

(15) Nb(CHCMe$_3$)(dmpe)Cl$_3$. A solution of dmpe (0.15 g) in 1 mL of $CHCl_3$ was added dropwise with stirring to Nb(CH$_2$CMe$_3$)$_2$Cl$_3$ (0.34 g) in 5 mL of $CHCl_3$ at −30 °C. The solution was warmed to room temperature and filtered, and the solvent was removed from the filtrate in vacuo to give a green solid which was recrystallized from toluene; yield 0.26 g (62%).

^{1}H NMR ($CDCl_3$): τ 6.21 (br d, 1, $^3J_{HP'}$ = 11 Hz, C*H*CMe$_3$), 7.95 (m, 4, PC*H*$_2$C*H*$_2$P), 8.60 (m, 12, −PMe$_2$), 8.89 (s, 9, CHC*Me*$_3$).

(16) [Ta(CHCMe$_3$)(PMe$_3$)Cl$_3$]$_2$. (a) From Ta(CH$_2$CMe$_3$)$_2$(PMe$_3$)Cl$_3$. An undisturbed, saturated ether solution of Ta(CH$_2$CMe$_3$)$_2$(PMe$_3$)Cl$_3$ (2.50 g) after 1 day at 25 °C yielded 1 equiv of CMe$_4$/1 equiv of Ta and large red crystals of [Ta(CHCMe$_3$)(PMe$_3$)Cl$_3$]$_2$ which were collected by filtration, rinsed with pentane, and dried in vacuo.

(b) From Ta(CH$_2$CMe$_3$)$_2$Cl$_3$ and Ta(CHCMe$_3$)(PMe$_3$)$_2$Cl$_3$. A solution of Ta(CH$_2$CMe$_3$)$_2$Cl$_3$ (2.58 g) in 5 mL of ether was added to Ta(CHCMe$_3$)(PMe$_3$)$_2$Cl$_3$ (3.06 g) in 20 mL of ether, and the mixture was left undisturbed for 24 h. Large red crystals were then isolated by filtration.

Anal. Calcd for $TaC_8H_{19}Cl_3P$: C, 22.17; H, 4.41. Found: C, 22.68; H, 4.28. ^{1}H NMR (C_6D_6): τ 4.70 (br s, 1, C*H*CMe$_3$), 8.86 (d, 9, $^2J_{HP}$ = 9.6 Hz, PMe$_3$), 8.90 (s, 9, CHC*Me*$_3$). ^{13}C NMR (C_6D_6): 276.0 (dd, J_{CH} = 101 Hz, $^2J_{CP}$ = 7 Hz, *C*HCMe$_3$), 46.6 (s, CH*C*Me$_3$), 33.5 (q, J_{CH} = 126 Hz, CHC*Me*$_3$), 15.8 ppm (qd, J_{CH} = 132 Hz, J_{CP} = 29 Hz, PMe$_3$). ^{31}P{^{1}H} NMR ($C_6D_5CD_3$, −30 °C, 36.43 MHz): 5.3 ppm (s). IR (Nujol/NaCl): 2605 (br, w, ν_{CH_a}) cm^{-1}. M_r (C_6H_6, 4.22 mM): calcd 868; found 853.

(17) [Ta(CHCMe$_3$)(PPhMe$_2$)Cl$_3$]$_2$. PPhMe$_2$ (0.25 g) in 2 mL of pentane was added dropwise with stirring to Ta(CH$_2$CMe$_3$)$_2$Cl$_3$ (0.86 g) in 10 mL of pentane at −30 °C. The color of the solution changed from yellow to red. On warming the solution to room temperature a red oil formed which crystallized after scratching the walls of the flask.

^{1}H NMR (C_6D_6): τ 2.6–3.1 (m, 5, Ph), 4.67 (br s, 1, C*H*CMe$_3$), 8.54 (d, 6, J_{HP} = 8.3 Hz, PPh*Me*$_2$), 8.92 (s, 9, CHC*Me*$_3$). IR (Nujol/NaCl): 2592 (m, ν_{CH_a}) cm^{-1}.

(18) [Ta(CHCMe$_3$)(PPh$_2$Me)Cl$_3$]$_2$. A procedure similar to the above employing 0.36 g of PPh$_2$Me at 25 °C gave 0.93 g of product after leaving the solution undisturbed overnight.

^{1}H NMR (C_6D_6): τ 2.6–3.1 (m, 5, Ph), 4.49 (s, 1, C*H*CMe$_3$), 8.12 (d, 3, $^2J_{HP}$ = 8.0 Hz, PPh$_2$*Me*), 8.90 (s, 9, CHC*Me*$_3$).

(19) [Ta(CHCMe$_3$)(PMe$_3$)Br$_3$]$_2$. PMe$_3$ (0.15 g) in 2 mL of ether was added dropwise with stirring to Ta(CH$_2$CMe$_3$)$_2$Br$_3$ (1.13 g) in 5 mL of ether at −30 °C. The yellow solution immediately became dark red and was allowed to warm to room temperature. Large crystals formed after leaving the solution undisturbed overnight. A second crop was collected from the mother liquor after half of the ether was removed in vacuo.

^{1}H NMR ($CDCl_3$): τ 6.16 (br s, 1, C*H*CMe$_3$), 8.22 (d, 9, $^2J_{HP}$ = 90 Hz, PMe$_3$), 8.73 (s, 9, CHC*Me*$_3$). ^{13}C NMR ($CDCl_3$): 283.0 (dd, J_{CH} = 86 Hz, $^2J_{CP}$ = 10 Hz, *C*HCMe$_3$), 47.9 (s, CH*C*Me$_3$), 33.3 (q, J_{CH} = 126 Hz, CHC*Me*$_3$), 17.7 ppm (qd, J_{CH} = 131 Hz, J_{CP} = 29 Hz, PMe$_3$). ^{31}P{^{1}H} NMR ($CHCl_3$, −50 °C, 36.43 MHz): 6.1 ppm (s). IR (Nujol/NaCl): 2519 (vw, ν_{CH_a}) cm^{-1}.

(20) [Nb(CHCMe$_3$)(PMe$_3$)Cl$_3$]$_2$. PMe$_3$ (0.14 g) in 1 mL of pentane was added dropwise with stirring to Nb(CH$_2$CMe$_3$)$_2$Cl$_3$ (0.68 g) in 5 mL of pentane at −30 °C. Red-brown crystals (probably Nb(CH$_2$CMe$_3$)$_2$(PMe$_3$)Cl$_3$) formed initially but dissolved in ca. 2 min to give a dark red solution containing a brown precipitate. The precipitate was filtered off immediately, rinsed with pentane, and extracted with minimal toluene. About an equal volume of pentane was added, and the solution was cooled to −30 °C to give red-purple crystals, yield 0.42 g (68%). The product appears to be slightly unstable and should be stored at −30 °C.

This compound can also be prepared in ca. 50% yield from Nb(CH$_2$CMe$_3$)$_2$Cl$_3$ and Nb(CHCMe$_3$)(PMe$_3$)$_2$Cl$_3$ in ether and purified as above.

^{1}H NMR (C$_6$D$_6$): τ 3.64 (br s, 1, C*H*CMe$_3$), 8.92 (d, 9, $^2J_{HP}$ = 10.3 Hz, PMe$_3$), 8.96 (s, 9, CHC*Me*$_3$). IR (Nujol/NaCl): 2595 (w, ν_{CH_α}) cm^{-1}.

(21) [Nb(CHCMe$_3$)(PPhMe$_2$)Cl$_3$]$_2$. PPhMe$_2$ (0.25 g) in 2 mL of pentane was added dropwise with stirring to Nb(CH$_2$CMe$_3$)$_2$Cl$_3$ (0.86 g) in 10 mL of pentane at −30 °C to give a purple-brown powder which was purified as above; yield 0.45 g (60%). The product should be stored at −30 °C.

^{1}H NMR (C$_6$D$_6$): τ 2.65–3.00 (m, 5, Ph), 3.62 (br s, 1, C*H*CMe$_3$), 8.43 (d, 6, $^2J_{HP}$ = 8.8 Hz, PPh*Me*$_2$), 8.89 (s, 9, CHC*Me*$_3$).

(22) Ta(CHSiMe$_3$)(PMe$_3$)$_2$Cl$_3$. PMe$_3$ (0.95 g) in 3 mL of CHCl$_3$ was added dropwise with stirring to Ta(CH$_2$SiMe$_3$)$_2$Cl$_3$ (2.31 g) in 15 mL of CHCl$_3$ at room temperature. The yellow solution slowly became deep red. After 8 h the solvent was removed in vacuo to give a green solid. This was dissolved in ether and the solution was filtered. The product was crystallized from the concentrated ether solution at −30 °C to give green crystals. A second crop was obtained by adding pentane to the mother liquor and standing the solution at −30 °C overnight.

^{1}H NMR (C$_6$D$_6$): τ 8.70 (br, 19, P*Me*$_3$), 9.70 (s, 9, CHSi*Me*$_3$). ^{13}C NMR (CDCl$_3$): 277.8 (d, J_{CH} = 101 Hz, *C*HSiMe$_3$), 15.8 (q, J_{CH} = 131 Hz, P*Me*$_3$), 3.2 ppm (q, J_{CH} = 119 Hz, CHSi*Me*$_3$).

(23) Ta(CH$_2$Ph)$_2$Br$_3$. A solution of Zn(CH$_2$Ph)$_2$ (2.48 g, 10.0 mmol) in toluene (20 mL) was added dropwise over 50 min to a stirred suspension of TaBr$_5$ (5.80 g, 10.0 mmol) in a mixture of toluene (125 mL) and ether (30 mL). The mixture was stirred 30 min and filtered. Removal of solvent from the filtrate left 5.00 g of brick-red crystals (83% yield).

^{1}H NMR (C$_6$D$_6$): τ 6.69 (s, 2, CH$_2$), 2.65–3.07 (m, 5, Ph). ^{13}C NMR (CDCl$_3$): δ 98.9 (t, $^1J_{CH}$ = 137 Hz, C$_\alpha$), 125.6 (s, C$_\beta$), 128.8 and 139.9 (overlapping C$_{ortho}$, C$_{meta}$, and C$_{para}$).

(24) Ta(CH$_2$Ph)$_2$(PMe$_3$)Cl$_3$. PMe$_3$ (0.36 g, 4.7 mmol) was added to Ta(CH$_2$Ph)$_2$Cl$_3$ (2.35 g, 5 mmol) in benzene (15 mL). After 1 min, 45 mL of pentane was added. After 15 min, brick-red crystals (2.13 g) were filtered off, washed with pentane, and dried in vacuo. A second crop (0.23 g) was obtained after standing the filtrate at room temperature for 1 h.

Anal. Calcd for TaC$_{17}$H$_{23}$Cl$_3$P: C, 37.42; H, 4.26. Found: C, 37.74; H, 4.35. ^{1}H NMR (C$_6$D$_6$): τ 8.85 (d, 9, $^2J_{HP}$ = 9 Hz, PMe$_3$), 6.80 (s, 4, CH$_2$), 2.60–3.08 (m, 10, Ph). ^{1}H NMR (CDCl$_3$, 270 MHz, −45 °C): τ 8.157 (d, $^2J_{HP}$ = 9 Hz, PMe$_3$), 6.657 (d, $^3J_{HP}$ = 11 Hz, CH$_2$), 2.5–3.3 (m, Ph). ^{13}C NMR (CDCl$_3$): δ 14 (dq, $^1J_{CP}$ = 20 Hz, J_{CH} = 125 Hz, PMe$_3$), 82 (q, $^1J_{CH}$ = 133 Hz, C$_\alpha$), 128 (overlapping d, $^1J_{CH}$ = 160 Hz, C$_{ortho}$ and C$_{meta}$), 136 (d, $^1J_{CH}$ = 160 Hz, C$_{para}$), 139 (s, C$_{ipso}$). ^{31}P NMR (CDCl$_3$, −45 °C): δ −3.8 (s).

(25) Ta(CHPh)(PMe$_3$)$_2$Cl$_3$. A benzene solution of Ta(CH$_2$Ph)$_2$Cl$_3$ (2.35 g, 5.00 mmol) and PMe$_3$ (1.18 g, 15.5 mmol) turned from deep red to forest-green after 1 h at 25 °C, and some green crystals had formed. The solution was then heated at 55 °C for 45 min and stood at room temperature for 8 h. Small green crystals (1.84 g) were filtered off, and pentane (ca. 80 mL) was added to the filtrate. After 15 min, a second crop of crystals (0.25 g) was isolated. Both crops were washed with benzene and pentane and dried in vacuo; total = 2.09 g (79% yield). The volatiles from a 4.4 mmol preparation were collected in a cold trap and 4.7 mmol of octane added as an internal standard; GLC analysis showed that 4.7 mmol of toluene was formed (1.1 mmol per tantalum). The rate of formation of Ta(CHPh)(PMe$_3$)$_2$Cl$_3$ is faster in dichloromethane but isolating a crystalline product seems more difficult. Ta(CHPh)(PMe$_3$)$_2$Cl$_3$ is only slightly soluble in benzene, more soluble in ether, and quite soluble in dichloromethane or chloroform.

Anal. Calcd for TaC$_{13}$H$_{24}$Cl$_3$P$_2$: C, 29.48; H, 4.58. Found: C, 29.47; H, 4.58. ^{1}H NMR (CDCl$_3$): τ 8.35 (br s, 18, PMe$_3$), 2.40–3.20 (m, 6, Ph and H). ^{1}H NMR (CDCl$_3$, 270 MHz, −40 °C; see Figure 3): τ 8.39 and 8.50 (each a doublet, $^3J_{HP}$ = 9 and 7 Hz, respectively; PMe$_3$ and PMe$_3$′ of cis,*mer* isomer), 8.26 (1:2:1 triplet, $J_{HP} \approx 4$ Hz, PMe$_3$ of trans,*mer* isomer), 4.57 (s, H$_\alpha$ of cis,*mer* isomer), 3.37 (m, H$_{para}$ of both isomers), 3.06 (m, H$_{ortho}$ of both isomers), 2.86 (m, H$_{meta}$ of both isomers), 2.60 (s, H$_\alpha$ of trans,*mer* isomer); trans,*mer*/cis,*mer* ratio is 3.5. ^{13}C NMR (CDCl$_3$, 67.89 MHz, −40 °C; see Figure 1 for part of ^{13}C{^{1}H} NMR spectrum): δ 14.9 (1:2:1 t, $J_{CP} \approx 13$ Hz, PMe$_3$ of trans,*mer* isomer), 12.8 and 16.9 (each a doublet, $^2J_{CP}$ = 18 and 27 Hz, respectively, PMe$_3$ and PMe$_3$′ of cis,*mer* isomer), 126.2–131.3 (overlapping phenyl C$_{ortho}$, C$_{meta}$, and C$_{para}$ resonances for both isomers), 142.8 (s, C$_\beta$ of trans,*mer* isomer), 149.6 (s, C$_\beta$ of cis,*mer* isomer), 234.5 (ddd, $^1J_{CH_\alpha}$ = 79 Hz, $^2J_{CP}$ = 15 Hz, $^2J_{CP'}$ = 33 Hz, C$_\alpha$ of cis,*mer* isomer), 244.2 (dt, $^1J_{CH_\alpha}$ = 90 Hz, $^2J_{CP}$ = 9 Hz, C$_\alpha$ of trans,*mer* isomer). ^{31}P NMR (see Figure 2). IR (Nujol): 2680 (m, v br, ν_{CH_α}) cm^{-1}.

(26) Ta(CHPh)(PMe$_3$)$_2$Br$_3$. An initially deep red mixture of Ta(CH$_2$Ph)$_2$Br$_3$ (3.01 g, 5.00 mmol) and PMe$_3$ (1.14 g, 15 mmol) in benzene (15 mL) turned emerald green after 20 min and crystals formed. A first crop was isolated by filtration, washed with benzene and pentane, and dried in vacuo; weight = 1.55 g. Pentane was layered on top of the filtrate to a total volume of 50 mL, and the flask walls were scratched. After ca. 24 h, a second crop (0.77 g) was isolated, washed, and dried in the same manner; total = 2.32 g (70% yield). Ta(CHPh)(PMe$_3$)$_2$Br$_3$ has the same solubility characteristics as Ta(CHPh)(PMe$_3$)$_2$Cl$_3$. GLC analysis of the reaction volatiles showed that 1.0 equiv of toluene had formed.

^{1}H NMR (CDCl$_3$): τ 8.20 (br s, 18, PMe$_3$), 2.45–3.20 (m, 6, Ph and H$_\alpha$). ^{13}C NMR (CDCl$_3$, −45 °C): δ 16.2 (br s, PMe$_3$), 126–131 (phenyl C$_{ortho}$, C$_{meta}$, and C$_{para}$ for both isomers), 143 (s, C$_\beta$ of trans,*mer* isomer), 237 (br m, C$_\alpha$ of cis,*mer* isomer), 240 (br s, $^1J_{CH_\alpha}$ = 83 Hz, C$_\alpha$ of trans,*mer* isomer; the trans,*mer*/cis,*mer* ratio is ca. 7). ^{31}P NMR (CDCl$_3$, −40 °C): δ −26 and −4 (d, $^2J_{PP'}$ = 12 Hz, PMe$_3$ and PMe$_3$ of cis,*mer* isomer), 0 (br s, PMe$_3$ of trans,*mer* isomer). IR (Nujol): 2570 (m, br, ν_{CH_α}) cm^{-1}.

(27) Ta(CHCMe$_3$)(THF)$_2$Cl$_3$. THF (1.44 g) in 2 mL of ether was added dropwise with stirring to Ta(CH$_2$CMe$_3$)$_2$Cl$_3$ (2.15 g) in 20 mL of ether at −30 °C. The color of the solution changed from yellow to red and then slowly to purple after the solution had warmed to 25 °C. After 8 h at room temperature the solution was filtered, and the volume of the solution was reduced in vacuo. Violet crystals formed after standing the concentrated ether solution at −30 °C for several days; yield 2.16 g (86%).

^{1}H NMR (CDCl$_3$, 35 °C): τ 5.67 (m, 8, $\overline{OCH_2CH_2CH_2CH_2}$), 6.50 (s, 1, C*H*CMe$_3$), 7.89 (m, 8, $\overline{OCH_2CH_2CH_2CH_2}$), 8.76 (s, 9, CHC*Me*$_3$). ^{13}C NMR (CDCl$_3$, −30 °C, 15 MHz, ^{1}H-gated decoupled): δ 253.8 (d, J_{CH} = 79 Hz, *C*HCMe$_3$), 79.7 (t, J_{CH} = 152 Hz, $\overline{OCH_2CH_2CH_2CH_2}$), 70.1 (t, J_{CH} = 150 Hz, $\overline{OCH_2CH_2CH_2CH_2}$), 44.9 (s, CHCMe$_3$), 32.8 (q, J_{CH} = 125 Hz, CHC*Me*$_3$), 25.7 (t, J_{CH} = 133 Hz, $\overline{OCH_2CH_2CH_2CH_2}$), 24.7 (t, J_{CH} = 133 Hz, $\overline{OCH_2CH_2CH_2CH_2}$). IR (Nujol): 2540 (w, ν_{CH_α}) cm^{-1}.

(28) Nb(CHCMe$_3$)(THF)$_2$Cl$_3$. The method is the same as in preparation 27.

^{1}H NMR (CDCl$_3$, −30 °C): τ 5.50 (m, 4, $\overline{OCH_2CH_2CH_2CH_2}$), 5.82 (m, 4, $\overline{OCH_2CH_2CH_2CH_2}$), 6.40 (br s, 1, C*H*CMe$_3$), 7.76 (m, 4, $\overline{OCH_2CH_2CH_2CH_2}$), 8.01 (m, 4, $\overline{OCH_2CH_2CH_2CH_2}$), 8.75 (s, 9, CHC*Me*$_3$). ^{13}C NMR (CDCl$_3$, −20 °C, 15 MHz, ^{1}H-gated decoupled): δ 257.0 (d, J_{CH} = 82 Hz, *C*HCMe$_3$), 78.4 (t, J_{CH} = 150 Hz, $\overline{OCH_2CH_2CH_2CH_2}$), 69.8 (t, J_{CH} = 149 Hz, $\overline{OCH_2CH_2CH_2CH_2}$), 47.6 (s, CHCMe$_3$), 29.0 (q, J_{CH} = 129 Hz, CHC*Me*$_3$), 25.0 (t, J_{CH} = 125 Hz, $\overline{OCH_2CH_2CH_2CH_2}$), 24.2 (t, J_{CH} = 125 Hz, $\overline{OCH_2CH_2CH_2CH_2}$).

(29) Ta(CHCMe$_3$)(THF)$_2$Br$_3$. The method is the same as in preparation 27. The color is blue-purple.

^{1}H NMR (CDCl$_3$): τ 5.53 (m, 8, $\overline{OCH_2CH_2CH_2CH_2}$), 7.20 (s, 1, C*H*CMe$_3$), 7.90 (m, 8, $\overline{OCH_2CH_2CH_2CH_2}$), 8.63 (s, 9, CHC*Me*$_3$).

(30) Ta(CHCMe$_3$)(py)$_2$Cl$_3$. At −30 °C a solution of pyridine (0.55 g) in 2 mL of dichloromethane was added dropwise with stirring to Ta(CH$_2$CMe$_3$)$_2$Cl$_3$ (1.29 g) in 8 mL of CH$_2$Cl$_2$. The yellow solution became red. After 8 h at 25 °C the solvent was removed in vacuo to yield a purple solid which was recrystallized from a concentrated ether solution with pentane at −30 °C.

^{1}H NMR (CDCl$_3$): τ 0.78–2.75 (m, 10, py), 6.37 (s, 1, C*H*CMe$_3$), 8.77 (s, 9, CHC*Me*$_3$). ^{13}C NMR (CDCl$_3$, 28 °C, 15 MHz, ^{1}H-gated decoupled): δ 254.7 (d, J_{CH} = 78 Hz, *C*HCMe$_3$), 153.1 (dd, J_{CH} = 182 Hz, $^2J_{CH}$ = 9 Hz, py), 150.7 (dd, J_{CH} = 179 Hz, $^2J_{CH}$ = 7 Hz, py), 139.7 (dt, J_{CH} = 164 Hz, $^2J_{CH}$ = 6 Hz, py), 138.5 (dt, J_{CH} = 166 Hz, $^2J_{CH}$ = 6 Hz, py), 124.6 (dt, J_{CH} = 169 Hz, $^2J_{CH}$ = 6 Hz, py), 124.1 (dt, J_{CH} = 169 Hz, $^2J_{CH}$ = 6 Hz, py), 45.5 (s, =CHCMe$_3$), 33.2 (q, J_{CH} = 126 Hz, CHC*Me*$_3$).

(31) Nb(η^5-C$_5$H$_5$)(CHCMe$_3$)Cl$_2$. Nb(CHCMe$_3$)(THF)$_2$Cl$_3$ (2.07 g, 5.00 mmol) was dissolved in 25 mL of 80/20 % v/v of ether/THF. Sublimed TlCp (1.35 g, 5.00 mmol) was then added to the stirred solu-

tion. The reaction mixture stayed purple as the TlCp disappeared and TlCl precipitated. After 1.5 h the reaction was filtered to remove TlCl (1.25 g) and the solvent was removed in vacuo to give a crude purple solid. The crude product was recrystallized from toluene/pentane (1:4) at −30 °C; yield 1.17 g (78%). Its ^{1}H NMR spectrum was identical with that of a previously prepared sample.[3]

(32) Nb(η^5-C_5Me_5)(CHCMe$_3$)Cl$_2$. Nb(CHCMe$_3$)(THF)$_2$Cl$_3$ (1.24 g, 3.00 mmol) was dissolved in 15 mL of benzene. TlC_5Me_5 (1.02 g, 3.00 mmol, see preparation 33) in 5 mL of benzene was added dropwise with stirring. The reaction was stirred for 1 h, and the mixture was filtered to remove TlCl (0.71 g). The solvent was removed from the filtrate in vacuo to give 1.06 g of a purple oil. The oil was sublimed at 65 °C (0.01 μm) onto a 0 °C probe to give the product as purple microcrystals; yield 0.97 g (88%). On this scale the product can be obtained only in low yield (since it is extremely soluble in pentane) by dissolving the purple oil in minimal pentane and cooling to −30 °C for several days.

^{1}H NMR (C_6D_6): τ 4.26 (br s, 1, C*H*CMe$_3$), 8.05 (s, 15, C_5Me_5), 8.88 (s, 9, CHC*Me*$_3$). ^{13}C NMR ($C_6D_5CD_3$, −30 °C, 15 MHz, ^{1}H-gated decoupled): δ 250.2 (br d, J_{CH} = 91 Hz, *C*HCMe$_3$), 121.1 (s, C_5Me_5), 48.8 (s, CHC*Me*$_3$), 31.6 (q, J_{CH} = 126 Hz, CHC*Me*$_3$), 13.0 (q, J_{CH} = 127 Hz, C_5Me_5). IR (Nujol): 2455 (m, ν_{CH_a}) cm^{-1}.

(33) TlC_5Me_5. A mixture of 1.42 g of LiC_5Me_5[16] and 3.80 g of Tl_2SO_4 in 25 mL of THF was stirred for 3 days at 25 °C. All solids were filtered off and the solvent was removed in vacuo. The yellowish residue was sublimed at 70 °C (0.01 μm) to give a bright yellow solid (1.8 g) whose ^{1}H NMR spectrum showed it to be a ca. 1:3 mixture of TlC_5Me_5 (τ 7.80 (d, J_{HTl} = 18 Hz)) and $C_{10}Me_{10}$ (τ 8.2 (6), 8.3 (6), 8.8 (3)). Recrystallization from pentane at −30 °C yielded 0.4 g of dark yellow-orange, pure TlC_5Me_5.

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Stereoelectronic Properties of Metalloenzymes. 6. Effects of Anions and Ferricyanide on the Copper(II) Site of the Histidine and the Tryptophan Modified Forms of Galactose Oxidase

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Abstract: A study of the coordination chemistry of three chemically modified forms of the copper(II)-containing enzyme, galactose oxidase, has been carried out. Alkylation of one unique histidine residue by iodoacetamide yields an inactive enzyme which does not bind CN^- or F^-, a property characteristic of the native enzyme. Oxidation by *N*-bromosuccinimide in 5 mM acetate buffer produces an inactive enzyme which binds F^- and CN^- in a manner very similar to that of the unmodified enzyme. However, after oxidation in 100 mM acetate buffer, CN^- causes a chemical reduction and F^- interacts with the copper(II) ion only weakly. Apparently, the different ionic strengths of 5 and 100 mM acetate buffers allow two and three tryptophans, respectively, to be oxidized. Taken together, these results suggest that different factors affect anion and substrate binding and further suggest that different sites at the one copper(II) center take part in these two processes. The $Fe(CN)_6^{3-}$ ion interacts with all modified forms and the unmodified enzyme to produce similar changes in the optical spectra. However, the ESR spectrum does not disappear with either of the modified forms as has been observed for the unmodified galactose oxidase. This represents definitive evidence that the unique optical changes are not due to the presence of Cu(III) in galactose oxidase. The additional observation of organic radical signals in the ESR spectra of the modified forms in the presence of $Fe(CN)_6^{3-}$ suggest that the loss of the copper ESR signal in the native enzyme under similar conditions may be due to a magnetically coupled copper(II)–radical pair or perhaps a copper(II)–ferricyanide dimer pair.

Introduction

The enzyme galactose oxidase (D-galactose:O_2 oxidoreductase, EC 1.1.3.9, herein referred to as GOase) has recently been the subject of intense study to determine the role of the single type II copper atom in the catalytic mechanism. This enzyme is a single-chain protein of molecular weight 68 000 ± 3000 daltons[1] and catalyzes the reaction: D-galactose + O_2 → D-galactohexodialdose + H_2O_2.[2] From electron spin resonance (ESR),[3] circular dichroism (CD),[4] optical and ligand binding studies,[5] it has been suggested that the inner-sphere coordination of the copper consists of two nitrogen atoms and two oxygen atoms in a pseudo-square-planar array. The two nitrogen atoms have been assigned as histidine imidazoles[3] whereas one oxygen has been suggested to be an exchangeable water molecule or hydroxide ion.[6,7] The origin of the other oxygen atom has not been determined. Even though these studies have shed considerable light on the nature of the copper center, it is equally important to understand the role of other amino acid residues which contribute to the binding and catalysis occurring at the active site. They must be complementary to the coordination chemistry of the copper atom.

Recent chemical modifications of GOase have led to the identification of at least one tryptophan[8] and one histidine[9] residue

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