phenylhydrazones **24** and **25**. When rats were treated with NNN, 73–85% of the dose was excreted in the urine, but **20** and **21** were not detected. However, products of further oxidation of **20** and **21**, the keto acid **23**, hydroxy acid **26**, and lactone **27** were isolated. The formation of **20** and **21** in vitro is most readily explained by initial 2′-hydroxylation or 5′-hydroxylation of NNN, as indicated in Scheme IV. The metabolites **23**, **26**, and **27** were formed, at least partially, by metabolic oxidation of **20** and **21**. Pathways other than an initial α-hydroxylation of NNN could have been involved in the formation of **23**, **26**, and **27**, which are also observed in the metabolism of nicotine.[69]

The results of these in vitro and in vivo experiments demonstrate that both NPy and NNN undergo metabolic α-hydroxylation in the rat. The mutagenicity data discussed above are consistent with the involvement of α-hydroxylation as the critical step in the metabolic activation of NPy and NNN. Further evidence on the role of α-hydroxylation in the activation of these compounds is currently being sought through carcinogenicity studies of α-deuterated NNN derivatives and through studies of the binding of NPy and NNN to DNA and RNA of target tissues.

Prospects

The results described in this review indicate that the tobacco-specific carcinogens, NNN and NNK, may be causative factors in the various cancers associated with tobacco usage. These nitrosamines are derived predominantly from the major tobacco alkaloid, nicotine, by nitrosation during the curing and smoking of tobacco. Other tobacco alkaloids may also be precursors to carcinogenic nitrosamines. Since NNN and NNK form during curing, it is feasible to reduce their concentrations in tobacco by appropriate management of the curing and related processes. Formation during smoking can also be inhibited. The reduction of these and related nitrosamines in tobacco and tobacco smoke is one approach to reduce tobacco-related cancers.

A second approach begins with an understanding of the metabolic activation and detoxification of tobacco-specific nitrosamines. The enzymes that mediate these transformations can be induced or inhibited by environmental modifiers. Such modifiers may increase or decrease the carcinogenic effects of these nitrosamines. NNN and NPy, as well as NNK, all undergo metabolic α-hydroxylation which is a likely activation process. Specific induction of α-hydroxylation could lead to greater carcinogenic activity; the modifier causing this would act as a cocarcinogen. Similarly, specific inhibition of α-hydroxylation could have a protective effect against carcinogenesis by these nitrosamines. The identification of these modifiers through metabolic studies and bioassays is important for a more complete characterization of the causative factors in tobacco carcinogenesis and for the prevention of tobacco-related cancer.

Note Added in Proof. Recently *N*′-nitrosoanatabine, another tobacco-specific *N*-nitrosamine, has been identified in tobacco (0.6–13 ppm), cigarette smoke (0.33–4.6 μg/cig), and cigarette sidestream smoke (0.15–1.5 μg/cig).[70] Data on the carcinogenic activity of this nitrosamine are not yet available.

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Alkylidene Complexes of Niobium and Tantalum

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Complexes containing a heteroatom-substituted carbene ligand, such as $W(CO)_5[C(Ph)(OMe)]$, were first prepared by Fischer 15 years ago.[1] Hundreds are now known which contain metals from groups 6–8 (usually in a 0 or +1 formal oxidation state if the carbene is taken to be a neutral two-electron ligand).

By comparison, isolable complexes of carbenes which contain only C and H (primary and secondary alkylidene complexes[2]) are rare, possibly because alkylidene ligands are not "stabilized" by a heteroatom substituent and the complexes therefore are more reactive. They (especially primary alkylidene complexes) had been postulated for several years as intermediates in the decomposition of transition-metal alkyl complexes[3] and

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(1) For reviews see D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, **72**, 575 (1972), and F. A. Cotton and C. M. Lukehart, *Prog. Inorg. Chem.*, **16**, 243 (1972).

(2) The alkylidene nomenclature is a useful, less misleading alternative to the carbene nomenclature. An alkylidene is derived from an alkyl ligand by removing an α-hydrogen atom. A primary alkylidene is derived from a primary alkyl ligand, methylene being a unique member of this family. A secondary alkylidene (or disubstituted methylene) is derived from a secondary alkyl ligand.

(3) (a) R. R. Schrock and G. W. Parshall, *Chem. Rev.*, **76**, 243 (1976); (b) P. J. Davidson, M. F. Lappert, and R. Pearce, *ibid.*, **76**, 219 (1976).

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in catalytic reactions such as the Cu(I)-catalyzed formation of a cyclopropane from diazomethane and an olefin,[4] olefin metathesis,[5] the rearrangement of small-ring hydrocarbons,[6] and the reduction of CO by H_2.[7] But the three which had been isolated by 1974 [$Cr(CO)_5$(2,3-diphenylcyclopropenylidene),[8] $W(CO)_5(CPh_2)$,[9] and [$Fe(\eta^5\text{-}C_5H_5)(CO)_2$(benzocyclobutenylidene)]$^+$[10]] are all similar to Fischer-type carbene complexes in the sense that they are 18-electron species, contain a metal in formally the 0 or +1 oxidation state, have at least one "stabilizing" resonance form, and react with nucleophiles at C_α of the alkylidene ligand.

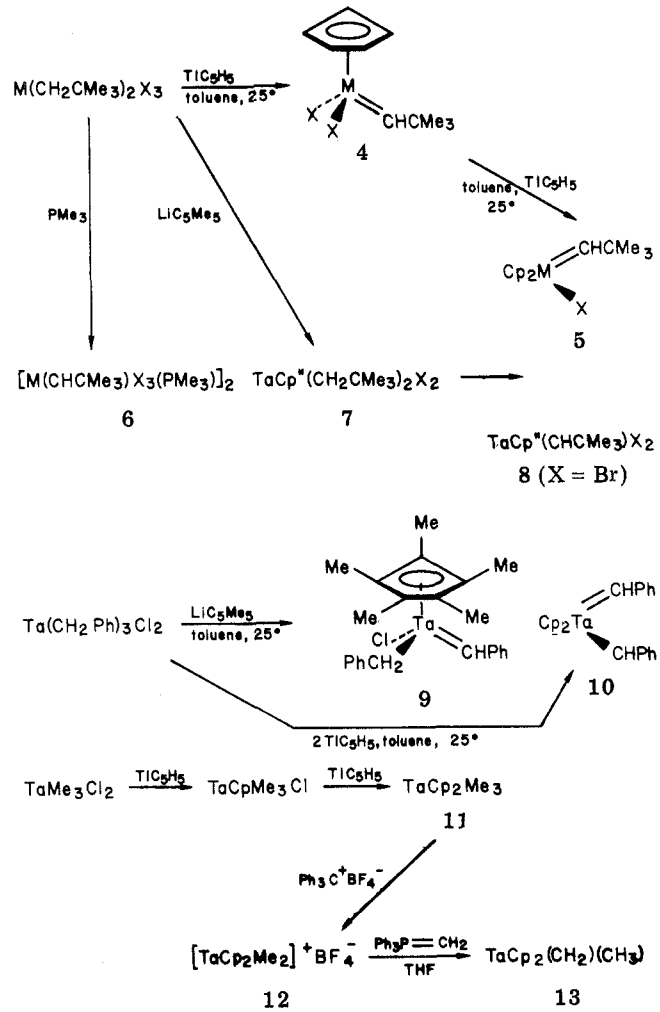
In 1974 a 10-electron Ta (formally 3+) neopentylidene complex was isolated as the product of decomposition of a Ta^{5+} neopentyl complex by loss of neopentane. This novel intramolecular "α-hydrogen abstraction" reaction has since been used to prepare a fairly large class of Ta (and Nb) neopentylidene and benzylidene complexes while an extension of the principle of α abstraction provided the first example of a stable transition-metal methylene complex. It thus became possible to structurally and spectroscopically characterize and systematically study the fundamental reactions of a number of related Nb and Ta alkylidene complexes. In the process we have begun to understand some aspects of the α-abstraction process by which they are formed, why they are stable, how these findings relate to the chemistry of other transition-metal alkyl complexes, and to what extent this chemistry is related to that of the main group cousins of Nb and Ta, namely, P, As, and Sb.

Preparation of Monoalkylidene Complexes

One would expect the reaction between $Ta(CH_2CMe_3)_3Cl_2$ and 2 mol of $LiCH_2CMe_3$ in pentane to give $Ta(CH_2CMe_3)_5$ based on similar preparations of $Ta(CH_2Ph)_5$ and $TaMe_5$.[11] Instead, sublimable, orange, crystalline **3** forms quantitatively[12] (eq 1). The most

$$\underset{\text{M = Nb or Ta}}{M(CH_2CMe_3)_3Cl_2} \xrightarrow[-LiCl]{LiCH_2CMe_3} \underset{\mathbf{1}}{M(CH_2CMe_3)_4Cl} \xrightarrow{-CMe_4} \underset{\mathbf{2}}{\text{“}(Me_3CCH_2)_2ClM{=}CHCMe_3\text{”}} \xrightarrow[-LiCl]{LiCH_2CH_3} \underset{\mathbf{3}}{M(CH_2CMe_3)_3(CHCMe_3)} \quad (1)$$

Scheme I
Some Preparations of Cyclopentadienyl/Alkylidene Complexes[a]



[a] Cp = η^5-C_5H_5, Cp″ = η^5-C_5Me_5, X = Cl or Br, M = Nb or Ta.

attractive postulate[12b] is that thermally unstable **1** forms in the first, relatively slow step of the reaction. It then "decomposes" by losing neopentane to give unstable **2** which reacts with $LiCH_2CMe_3$ to give **3**; both steps are fast relative to the first. The crucial α-hydrogen abstraction step (**1** → **2**) is discussed in detail later. One of the most important requirements is that the transition-metal alkyl precursor be a crowded molecule.

Substitution of a chloride ligand with an η^5-cyclopentadienyl ligand will induce α-hydrogen abstraction in neopentyl and benzyl complexes to give neopentylidene complexes (**4**,[13] **5**,[14] or **8**[15a]) or benzylidene complexes (**9**[16] or **10**[14]), respectively (Scheme I). The success of this approach depends on the type of cyclopentadienyl group; for example, $Ta(CH_2CMe_3)_2Cl_3$ and $C_5H_5^-$ give **4**, but with $C_5Me_5^-$, **7** is the product. It also depends on the halide; for example, **7** is a stable

(4) (a) W. Kirmse, "Carbene Chemistry", Vol. 1, Academic Press, New York and London, 1971, and references therein; (b) "Carbenes", Vol. 1, M. Jones, Jr., and R. A. Moss, Ed., Wiley-Interscience, 1973.
(5) (a) R. J. Haines and G. J. Leigh, *Chem. Soc. Rev.*, **4**, 155 (1975); (b) N. Calderon, E. A. Ofstead, and W. A. Judy, *Angew. Chem., Int. Ed. Engl.*, **15**, 401 (1976).
(6) (a) R. Noyori, T. Suzuki, Y. Kumagai, and H. Takaya, *J. Am. Chem. Soc.*, **93**, 5894 (1971); (b) R. Noyori, *Tetrahedron Lett.*, 1691 (1973), and references therein; (c) K. C. Bishop, III, *Chem. Rev.*, **76**, 461 (1976).
(7) (a) H. Pichler and H. Schultz, *Chem. Ing. Tech.*, **42**, 1162 (1970); (b) Y. T. Eidus, *Russ. Chem. Rev.*, **36**, 333 (1967); (c) M. A. Vannice, *Catal. Rev. Sci. Eng.*, **14**, 153 (1976); (d) H. H. Storch, N. Golumbic, and R. B. Anderson, "The Fischer-Tropsch and Related Synthesis", Wiley, New York, 1951.
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(14) R. R. Schrock, L. W. Messerle, C. D. Wood, and L. J. Guggenberger, *J. Am. Chem. Soc.*, **100**, 3793 (1978).
(15) (a) C. D. Wood, S. J. McLain, and R. R. Schrock, *J. Am. Chem. Soc.*, in press; (b) G. A. Rupprecht and R. R. Schrock, unpublished results.
(16) S. J. McLain, C. D. Wood, L. W. Messerle, R. R. Schrock, F. J. Hollander, W. J. Youngs, and M. R. Churchill, *J. Am. Chem. Soc.*, **100**, 5962 (1978).

Table I
Structural Data for 18-Electron Alkylidene Complexes

compound	Ta=C, A	Ta—C, A	θ, deg	$\Delta G^{\ddagger}_{rot}$, kcal mol^{-1}	$\angle MC_\alpha C_\beta$,[a] deg	$^1J_{CH_\alpha}$, Hz	$\angle MC_\alpha H_\alpha$, deg
$TaCp_2(CH_2)(CH_3)$[22]	2.026 (10)	2.246 (12)	88 (3)	≥ 21[14]	126 (4)[a]	132	126 (4)
$TaCp_2(CHPh)(CH_2Ph)$[14]	2.07 (1)	2.30 (1)	95.7 (5)	19.2[14]	135.2 (7)[b]	127	
$TaCp_2(CHCMe_3)Cl$[23]	2.030 (6)		79.7 (5)	16.8[14]	150.4 (5)[c]	121	111 (4)

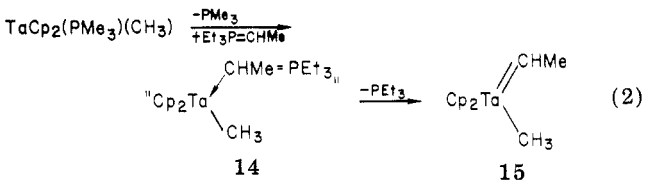
[a] In the CH_2 ligand, of course, "$\angle MC_\alpha C_\beta$" = $\angle MC_\alpha H_\alpha$. [b] For the benzyl ligand this angle is 123 (1)°. [c] For the neopentyl ligand in $Ta(CH_2CMe_3)_3(CCMe_3)$(Li·dimethylpiperazine) this angle is 128 (4)°.

product when X = Cl, but when X = Br, 7 → 8 quantitatively in a comparatively fast, smooth, first-order reaction.[15a]

Addition of a neutral ligand such as PMe_3 to an alkyl complex will also induce α-hydrogen abstraction. An example is **6**.[17] As we will see later, the primary role of PMe_3 (like a cyclopentadienyl ligand) is to create a crowded coordination sphere and/or a geometry in which α abstraction is easier.

In contrast, addition of one η^5-C_5H_5 to $TaMe_3Cl_2$ gives $TaCpMe_3Cl$, and addition of a second gives $TaCp_2Me_3$ (**11**). In fact, no example of a strictly thermally promoted α-abstraction reaction in a methyl complex to give a stable methylene complex (e.g., **11** → **13**) is known, partly because the methylene complex (e.g., **13**) decomposes as fast as it is formed (see below). This problem can be circumvented, however, by making use of the analogy between main-group and transition-metal group 5 elements. Treating **11** with trityl tetrafluoroborate gives the "tantalonium" salt **12**, which is deprotonated smoothly by a base (the cleanest of which is a phosphorane) to give **13** in high yield.[18] It is the only known transition-metal methylene complex.

By now the reader will have noticed that none of the alkyls we have mentioned (CH_3, CH_2Ph, or CH_2CMe_3) has any β-hydrogen atoms. What is known at present about decomposition of transition-metal alkyl complexes would lead one to predict that a β-hydrogen atom will always be lost more readily than an α-hydrogen atom,[3a] especially if the metal complex has less than an 18-valence-electron count. Hence techniques other than α abstraction or deprotonation must be used to prepare, for example, an ethylidene complex. Alkylidene transfer is potentially useful in this regard. The labile PMe_3 ligand in $TaCp_2(PMe_3)(CH_3)$ is replaced by $Et_3P{=}CHMe$ to form the postulated intermediate "ylide complex" **14**, which then loses PEt_3 to give **15**[19] (eq 2). Thus one could in theory prepare by this



14 15 (2)

method other complexes which probably could not be prepared by an α-abstraction route.

In general, these Nb and Ta alkylidene complexes react with even traces of oxygen or water (or other protic solvents), although sterically crowded 18-electron complexes like $TaCp_2(CHCMe_3)Cl$ can be handled as solids briefly in air. These are also the most stable thermally ($TaCp_2(CHCMe_3)Cl$ is stable in refluxing toluene). The least stable thermally are methylene complexes like **13** or relatively uncrowded complexes like **2**, probably since at least one decomposition pathway is bimolecular to form the olefin (see below). In general, Nb complexes appear to be less stable, thermally and hydrolytically, than their Ta analogues.

Spectroscopic Characterization

^{13}C NMR spectroscopy is invaluable for characterizing alkylidene complexes since the alkylidene C_α resonance invariably is found at low field (200–300 ppm downfield of Me_4Si). This large chemical shift appears to be characteristic of many types of carbon atoms which are multiply bonded to some extent to a transition metal[20] but for reasons which are not yet clear.[21] One important finding is that $^1J_{CH_\alpha}$ varies widely. Low values (75–100 Hz) are found in neopentylidene and benzylidene complexes which have less than 18 valence electrons (e.g., $Ta(\eta^5\text{-}C_5Me_5)(CHCMe_3)(CH_2CMe_3)Cl$ = 14 e, $^1J_{CH_\alpha}$ = 76 Hz[16]), while higher values (105–130 Hz) are found in the 18-electron complexes, $MCp_2(CHR)(X)$ (R = CMe_3, Ph, H; X = Cl, CH_2Ph, and CH_3, respectively[14]).

A second, potentially important result is that the location of the ^1H NMR signal for H_α varies from τ −2 to 12. It is found at lowest fields in the 18-electron complexes, $MCp_2(CHR)(X)$.

A third interesting feature is that the C–H_α stretching frequency is surprisingly low in the electron deficient (<18 e) complexes. In $TaCp(CHCMe_3)Cl_2$, for example, it is found at 2510 cm^{-1} (weak).[15a] A similar peak is found in the IR spectra of many other electron-deficient alkylidene complexes, but notably *not* in the spectra of the 18-electron complexes, $MCp_2(CHR)X$. A low value for ν_{CH_α} therefore correlates with a low value for $^1J_{CH_\alpha}$.

Structure and Bonding

The structures of three 18-electron complexes are known. $TaCp_2(CH_2)(CH_3)$[22] is shown in Figure 1. Some pertinent structural data for $TaCp(CH_2)(CH_3)$, and for the related molecules, $TaCp_2(CHPh)(CH_2Ph)$[14] and $TaCp_2(CHCMe_3)Cl$,[23] can be found in Table I.

The Ta=C(alkylidene) bond length is rather short in each case (~0.22 Å shorter than the respective Ta–C single bonds in the first two molecules) and suggestive of a significant amount of multiple bonding between Ta and C_α(alkylidene). Since the π-bonding orbital in

(17) A. J. Schultz, J. M. Williams, R. R. Schrock, G. A. Rupprecht, and J. D. Fellmann, *J. Am. Chem. Soc.*, in press.
(18) (a) R. R. Schrock, *J. Am. Chem. Soc.*, **97**, 6577 (1975); (b) R. R. Schrock and P. R. Sharp, *ibid.*, **100**, 2389 (1978).
(19) P. R. Sharp and R. R. Schrock, *J. Organometal. Chem.*, in press.
(20) M. H. Chisholm and S. Godleski, *Prog. Inorg. Chem.*, **20**, 299 (1976).
(21) J. Evans and J. R. Norton, *Inorg. Chem.*, **13**, 3042 (1974).
(22) L. J. Guggenberger and R. R. Schrock, *J. Am. Chem. Soc.*, **97**, 6578 (1975).
(23) (a) M. R. Churchill, F. J. Hollander, and R. R. Schrock, *J. Am. Chem. Soc.*, **100**, 647 (1978); (b) M. R. Churchill and F. J. Hollander, *Inorg. Chem.*, **17**, 1957 (1978).

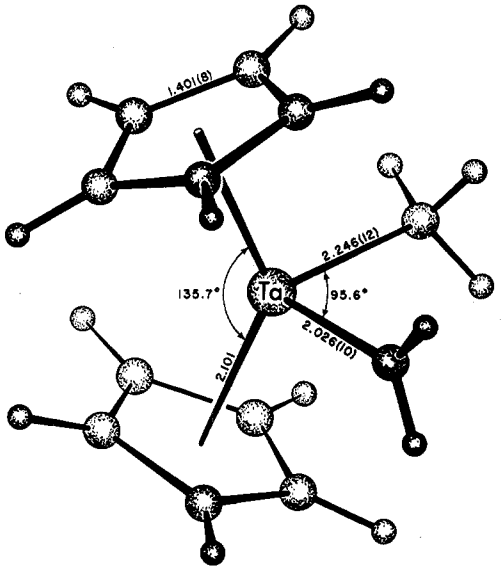


Figure 1. The molecular structure of $Ta(\eta^5\text{-}C_5H_5)_2(CH_2)(CH_3)$.

"bent" bis(cyclopentadienyl) complexes lies in the plane passing between the two Cp rings,[24] the alkylidene ligand must be oriented perpendicular to that plane (θ = 90°) in order to allow overlap of the metal π orbital with the carbon $2p_z$ orbital. This is sterically possible only for the methylene ligand (θ = 88 ± 3°; Table I). The phenyl ring of the benzylidene ligand is turned *toward* the $-CH_2Ph$ ligand (θ = 96°) while the *tert*-butyl group in the neopentylidene ligand is turned *away* from the chloride (θ = 80°). Interestingly, the methylene ligand does not readily turn into the plane but the benzylidene and neopentylidene ligands do, with $\Delta G^{\ddagger}_{rot}$ values which are inversely proportional to the extent which the alkylidene ligand planes deviate from the perpendicular (6 and 10°, respectively). *If we assume* that the different $\Delta G^{\ddagger}_{rot}$ values reflect energy differences in the *ground* state rather than the *transition* state with =CHR "in the plane", then we can make two statements. The fact that $\Delta G^{\ddagger}_{rot}$ is so sensitive to how much θ deviates from 90° suggests that the overlap between metal and carbon π-type orbitals is poor. Secondly, since there is arguably no orthogonal π-bonding orbital of relatively low energy in MCp_2L_2 species,[24] the maximum value for $\Delta G^{\ddagger}_{rot}$ is an *approximate* measure of the strength of the metal–alkylidene π bond. We estimate this to be 25 kcal mol^{-1}.[25] Ta–C single bond strengths are on the order of 40–60 kcal mol^{-1}.[3a] Therefore the total alkylidene–metal bond strength (ΔH for dissociation to give a free carbene) is on the order of at least 75 kcal mol^{-1}.

The alkylidene $Ta\text{–}C_\alpha\text{–}C_\beta$ angles in $TaCp_2(CHPh)(CH_2Ph)$ and $TaCp_2(CHCMe_3)Cl$ are progressively larger than might be expected for an sp^2-hybridized C_α (Table I). Presumably steric factors play a significant role in opening up this angle in =CHR complexes as the size of R increases. A consequence is that $M\text{–}C_\alpha\text{–}H_\alpha$ must decrease. Interestingly, so does $^1J_{CH_\alpha}$ (Table I).

The structure of $[Ta(CHCMe_3)Cl_3(PMe_3)]_2$ (14 valence electrons per Ta, $^1J_{CH_\alpha}$ = 101 Hz, ν_{CH_α} = 2605 cm^{-1}), as determined by neutron diffraction techniques,

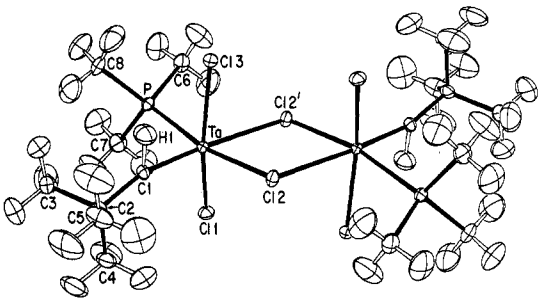
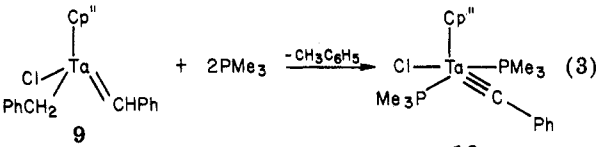


Figure 2. The molecular structure of $[Ta(CHMe_3)(PMe_3)Cl_3]_2$ with thermal ellipsoids scaled to 50% probability. Important interatomic distances (Å) are: Ta–C(1) = 1.898 (2), C(1)–H(1) = 1.131 (3), C(1)–C(2) = 1.501 (2), Ta···H(1) = 2.119 (4), Ta–Cl(2)′ = 2.815 (2), and Ta–Cl(2) = 2.448 (2). Important angles (deg) are: Ta–C(1)–C(2) = 161.2 (1), C(2)–C(1)–H(1) = 113.7 (2), Ta–C(1)–H(1) = 84.8 (2), C(1)–Ta–Cl(1) = 95.13 (7), and C(1)–Ta–Cl(3) = 104.01 (7). The dihedral angle between the C(1)–Ta–P plane and the C(2)–C(1)–H(1) plane is 89.8 (2)°.

is shown in Figure 2.[17] The $Ta\text{–}C_\alpha\text{–}C_\beta$ angle is even larger (161°), and the $Ta\text{–}C_\alpha\text{–}H_\alpha$ angle *less than 90°* (85°). The $=C\text{—}H_\alpha$ bond length (1.131 (3) Å) is slightly longer than that predicted[26] (1.120 Å) for a pure C(2p)–H(1s) bond, and much longer than a C(sp^2)–H(1s) bond. This reasonably explains the low values for $^1J_{CH_\alpha}$ and ν_{CH_α}.[17] Surprisingly, the Ta=C bond is much shorter than in 18-electron complexes, not much longer, in fact, than the Ta≡C bond length found in an alkylidyne complex,[27] $Ta(\eta^5\text{-}C_5Me_5)(CPh)(PMe_3)_2Cl$ (1.849 (8) Å).[16] In short, the electron-deficient metal is attracting the $C\text{–}H_\alpha$ electron pair (the *electronic* effect) as the $M{=}C_\alpha\text{—}C_\beta$ angle increases in a crowded molecule (the *steric* effect); the two operate synergistically in electron-deficient (less than 18 electron) complexes, but only the latter can operate in 18-electron complexes such as $MCp_2(CHR)X$. In the extreme the $M{=}CH_\alpha$ bond might be best described as an asymmetric, 3-center, 6-electron bond containing a "semibridging" α-hydrogen atom. We can now understand how an alkylidene α-hydrogen atom can be removed to give the alkylidyne complex mentioned above (eq 3); the $C\text{–}H_\alpha$ bond strength is low[26] and/or



the acidity of H_α is enhanced. This too is a type of α-abstraction reaction, one which almost certainly is related to the one by which the alkylidene formed from the alkyl (vide infra).

Reactions

Fischer-type carbene complexes (and $W(CO)_5(CPh_2)$[9,29a] and $W(CO)_5(CHPh)$[29b]) behave as electro-

(24) (a) L. J. Guggenberger, *Inorg. Chem.*, **12**, 294 (1973); (b) J. L. Petersen and L. F. Dahl, *J. Am. Chem. Soc.*, **97**, 6416 (1975); (c) J. W. Lauher and R. Hoffman, *ibid.*, **98**, 1729 (1976).

(25) Lauher and Hoffman[24c] estimated $\Delta G^{\ddagger}_{rot}$ in hypothetical $[TiCp_2(CH_2)(CH_3)]^-$ to be ~27 kcal mol^{-1}.

(26) C. A. Coulson, "Valence", 2nd ed., Oxford University Press, London, 1963, p 210.

(27) (a) The first alkylidyne complexes were of the type *trans*-$Br(CO)_4W{\equiv}C\text{—}C_6H_5$ and were prepared by removing (formally) a nucleophile (RO^-) from the α-carbon atom of a Fischer-type carbene complex.[28] As we shall see shortly this is yet another indication that Fischer-type carbene complexes and the alkylidene complexes discussed here are rather different. (b) See also L. J. Guggenberger and R. R. Schrock, *J. Am. Chem. Soc.*, **97**, 2935 (1975).

(28) E. O. Fischer and U. Schubert, *J. Organometal. Chem.*, **100**, 59 (1975).

philes at C_α. However, C_α in the Nb and Ta alkylidene complexes is nucleophilic; they are therefore related to main group ylides of P and As.[29c] For example, **13** forms an adduct with $AlMe_3$ [**17**; cf. $Me_3P{=}CH_2 + AlMe_3 \rightarrow Me_3PCH_2AlMe_3$[30]], but not with PMe_3,[29a] and reacts to give the expected products of S_N2 reactions, **18** and (ultimately) **19** (eq 4). Accordingly, all alkylidene

$$\underset{\mathbf{13}}{TaCp_2(CH_2)(CH_3)} \xrightarrow{AlMe_3} \underset{\mathbf{17}}{TaCp_2(CH_2AlMe_3)(CH_3)} \xrightarrow{Me_3SiBr} \underset{\mathbf{18}}{[TaCp_2(CH_2SiMe_3)(CH_3)]^+Br^-} \xrightarrow{CD_3I} \text{"}TaCp_2(CH_2CD_3)(CH_3)I\text{"} \xrightarrow{-CH_3D} \underset{\mathbf{19}}{TaCp_2(CH_2CD_2)I} \quad (4)$$

ligands bound to Nb and Ta protonate at C_α, e.g., **3** + HCl → **1** (eq 1).

Reactions of **3** with the carbonyl function in ketones and aldehydes[31] parallel the Wittig reaction[32] in that both cis and trans olefins are formed and the reaction

$$\underset{\mathbf{3}}{(Me_3CCH_2)_3M{=}CHCMe_3} + R'COR'' \xrightarrow[25\ ^\circ C]{pentane} \textit{cis}\text{- and }\textit{trans}\text{-}R'R''C{=}CHCMe_3 + [(Me_3CCH_2)_3Ta(O)]_x \quad (5)$$

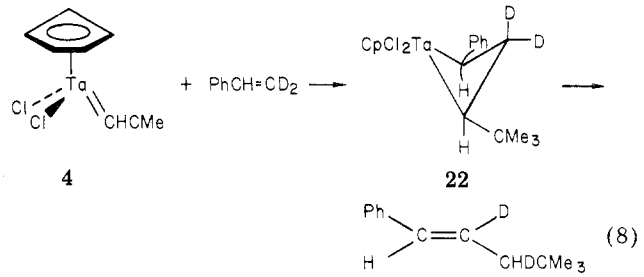
slows markedly if the carbonyl function is sterically inaccessible ($PhCOCH_3$ reacts instantaneously at 25 °C, Me_3CCHO negligibly in 6 h). The metal oxide product is a polymer, presumably because of the greater affinity (compared to P) of Nb and Ta for oxygen. This is probably also the reason why *esters* and even *amides* react similarly to give vinyl ethers and enamines, a reaction which is virtually unknown in phosphorus ylide chemistry.[32]

Acid chlorides and nitriles react with alkylidene complexes to give products like **20**[12b] (eq 6) or **21**[15a] (eq 7). These results are consistent with C_α being nucleophilic but also demonstrate that Nb and Ta prefer to bond to more electronegative N and O rather than to carbon. The first interaction therefore could equally likely be electrophilic attack by the metal on O or N in the ketone or nitrile, respectively. Nucleophiles have room to and will add to $TaCp(CHCMe_3)Cl_2$; e.g., PMe_3 adds to give $TaCp(CHCMe_3)Cl_2(PMe_3)$, in which $^1J_{CH_\alpha}$ and ν_{CH_α} for the alkylidene ligand are virtually unchanged.[16]

$$(Me_3CCH_2)_3Nb{=}CHCMe_3 + CH_3C(O)Cl \rightarrow \underset{\mathbf{20}\ (E\text{ and }Z)}{(Me_3CCH_2)_3Nb(Cl)OC(CH_3){=}CHCMe_3} \quad (6)$$

$$TaCp(CHCMe_3)Cl_2 + PhC{\equiv}N \rightarrow \underset{\mathbf{21}\ (E\text{ and }Z)}{CpCl_2Ta{=}NC(Ph){=}CHCMe_3} \quad (7)$$

Ethylene, propylene, and styrene react readily with alkylidene complexes having less than 18 valence electrons such as **4** (eq 8).[13] We now believe the olefin

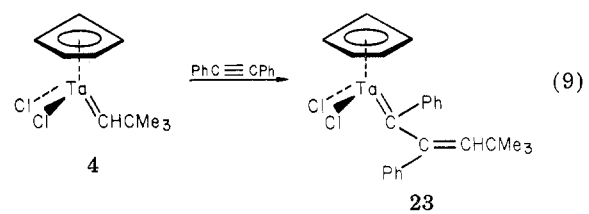


4 **22** (8)

coordinates to the electron-poor metal first. C_α then attacks one end of the bound olefin (olefins bound to later transition metals are attacked by nucleophiles) as a metal–carbon bond forms at the other end, to give a metallocyclobutane complex, **22** (a 14-electron complex). It loses a β-hydrogen atom to give (most likely) an η^1- or η^3-allyl hydride complex which reductively eliminates a new olefin.[33] ("β-Hydride elimination" is a common form of decomposition of metal alkyl complexes which contain one or more β-hydrogen atoms on the alkyl ligand(s).[3]). One olefin product predominates (90–95%) starting with **4**, but mixtures containing two or more possibilities are found starting with other alkylidene complexes such as **6**.[15b]

The most surprising aspect of this reaction is that, although metallocyclobutane complexes are postulated intermediates in olefin metathesis,[5] the metathesis product ($Me_3CCH{=}CD_2$ from **22**) is not found. Another possible product, a cyclopropane, also is not. Perhaps they would be if the β-elimination step in the metallocycle intermediate could be slowed down, for example, if the intermediate were an 18-electron species. This is possible starting with a member of the $MCp_2(CHR)X$ class, but these either decompose first (when R = H, see below) or are quite unreactive toward ordinary olefins, probably because the olefin cannot easily coordinate to the metal.

Acetylenes, like nitriles, "insert" into the M=CHR bond.[15a] The new ligand, a secondary alkylidene, must form by rearrangement of an intermediate metallocyclobut*ene* complex (e.g., **4** → **23**; one C=C isomer, eq 9). Further reaction of **23** with PhC≡CPh is slow



4 **23** (9)

for steric reasons, but probably also because the α-phenyl substituent mitigates the nucleophilicity of the α-carbon atoms in **23**.

Bis(alkylidene) Complexes

$Ta(CH_2CMe_3)_3(CHCMe_3)$ is thermally stable but loses neopentane readily on addition of PMe_3 to give

(29) (a) The electrophilic secondary alkylidene ligand in $(CO)_5W{=}CPh_2$ forms an adduct with PMe_3: F. R. Kreissl and W. Held, *J. Organomet. Chem.*, **86**, C10 (1975); (b) C. P. Casey and S. W. Polichnowski, *J. Am. Chem. Soc.*, **99**, 6097 (1977); (c) H. Schmidbaur, *Adv. Organometal. Chem.*, **14**, 205 (1976).

(30) H. Schmidbaur and W. Tronich, *Chem. Ber.*, **101**, 595 (1968).

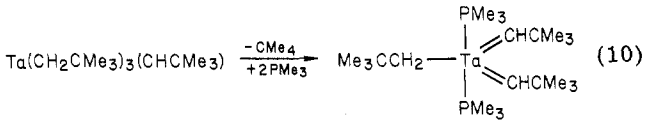
(31) R. R. Schrock, *J. Am. Chem. Soc.*, **98**, 5399 (1976).

(32) (a) G. Wittig, *J. Organomet. Chem.*, **100**, 279 (1975); (b) A. W. Johnson, "Ylid Chemistry", Academic Press, New York, 1966.

(33) The high yield organometallic product of these reactions is a metallocyclopentane complex[13] (from two ethylene or propylene molecules) or an olefin complex[15] (in the case of styrene). Dienes give tantallobicyclic complexes.[34]

(34) S. J. McLain and R. R. Schrock, *J. Am. Chem. Soc.*, **100**, 1315 (1978).

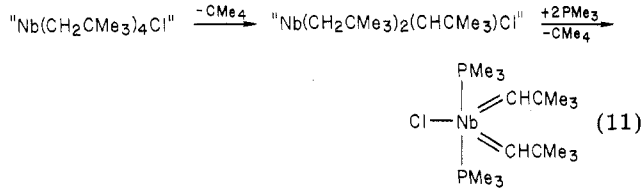
the bis(neopentylidene) complex, **24**[35] (eq 10). The



(10)

24

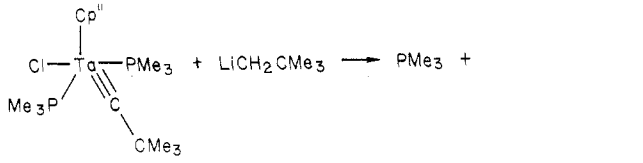
structure shown is the preferred alternative[35] since preliminary X-ray data confirm that trigonal-bipyramidal Ta(mesityl)$(CHCMe_3)_2(PMe_3)_2$ contains axial PMe_3 ligands.[36] Similar compounds (e.g., **25**, eq 11) are



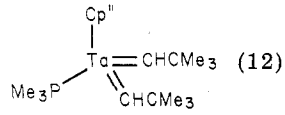
(11)

25

formed when $M(CH_2CMe_3)_4Cl$ decomposes to $M(CH_2CMe_3)_2(CHCMe_3)Cl$[12b] in the presence of PMe_3. In each case either a bis(neopentylidene) or a neopentyl/neopentylidyne complex could be the *first*-formed product since **16** reacts readily with $LiCH_2CMe_3$ to give free PMe_3 and **26** (eq 12).[35]



16



(12)

26

In each bis(neopentylidene) complex the two alkylidenes are nonequivalent in the ground-state structure and the PMe_3 ligands equivalent. Therefore the two alkylidene ligands must lie in the same plane (in **24** and **25** at least) and must point in the *same* direction.[36] In all three complexes the two neopentylidene ligands equilibrate at a rate which is on the order of the NMR time scale. Rotation about their M=C bonds is the most reasonable explanation.

Bis(alkylidene) complexes[37] are of theoretical as well as practical importance. One intriguing question is why **26** (for example) is not an olefin complex? The answer may be that Ta is so electron-poor it prefers the 16 valence electrons in **26** compared to the 14 valence electrons in the olefin complex. In that case (*if* intermolecular decomposition pathways can be prevented; see next section) even a bis(methylene) complex might be preparable. Perhaps the most interesting result, however, would be that as the size of the R substituent on =CHR decreases the olefin complex *does* form. To form a bis(alkylidene) complex *from* an olefin would then no longer seem implausible and would be potentially an intriguing new way of utilizing olefins in metal-catalyzed reactions (cf. olefin metathesis[5]).

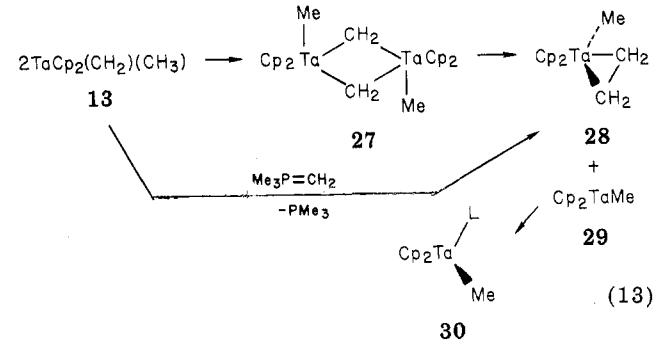
(35) J. D. Fellmann, G. A. Rupprecht, C. D. Wood, and R. R. Schrock, *J. Am. Chem. Soc.*, **100**, 5964 (1978).

(36) M. R. Churchill, private communication.

(37) Complexes containing two or even three highly stabilized Fischer-type carbene ligands such as $\overline{CNRCH_2CH_2NR}$ have been prepared; see, for example, M. F. Lappert and P. L. Pye, *J. Chem. Soc., Dalton Trans.*, 2172 (1977), and references therein.

Decomposition of Alkylidene Complexes

$TaCp_2(CH_2)(CH_3)$ (**13**) decomposes at a rate which is second order in Ta and zero order in an added ligand like PMe_3.[18b] The postulated intermediate, **27**, must cleave readily to give **28** and unstable **29** which is captured in the presence of L to give **30** (eq 13). A



(13)

30

L = PMe_3, CO, C_2D_4

similar intermediate may be formed in the reaction of **13** with its main group relative, $Me_3P{=}CH_2$, to give PMe_3 and **28**.[18b]

Bimolecular decomposition to give the olefin formed by coupling two alkylidene ligands[38] becomes less likely if the methylene ligand is substituted by a phenyl or *tert*-butyl group. Intramolecular α-hydrogen transfer pathways therefore become more important. Two possible products, alkylidyne complexes (or dimers thereof[40]) and bis(alkylidene) complexes, have already been mentioned.

As the coordination sphere becomes less crowded and/or ligands (e.g., tertiary phosphines) become labile, intermolecular reactions of a related, but more complex, nature than the intramolecular ones would seem more likely. A relatively simple example is shown in eq 14.

$$2Cl_xM{=}CHR \rightarrow Cl_{x+1}M{-}CH_2R + Cl_{x-1}M{\equiv}CR \quad (14)$$

However, redox processes also would now be more likely and could lead to considerably more complex results.

Rearrangement of an alkylidene ligand which has a β-hydrogen atom to an olefin would seem a likely decomposition path since this is a well-known type of rearrangement of free carbenes.[4] It is not facile in 18-electron complexes such as $TaCp_2(CHMe)Me$[19] or $MnCp(CO)_2(CMe_2)$[41a,b] although it is in the 18-electron complexes, $(CO)_5W{=}CPhMe$[41c,d] and $MnCp(CO)_2(CPhMe)$.[41d] Since the electron count does not change during the rearrangement process (cf. β-hydride elimination in alkyl complexes[3]), loss of a ligand from

(38) An olefin is always formed when Fischer-type carbene complexes decompose.[1] In at least one case[39] this has been shown to be an intermolecular reaction.

(39) C. P. Casey and R. L. Anderson, *J. Chem. Soc., Chem. Commun.*, 895 (1975).

(40) (a) Complexes containing "bridging alkylidyne" groups, $[M(CH_2SiMe_3)_2(CSiMe_3)]_2$ (M = Nb or Ta), are formed instead of the potential precursor, $M(CH_2SiMe_3)_3(CHSiMe_3)$, an analogue of **3**;[40b,c] (b) W. Mowat and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1120 (1973); (c) F. Huq, W. Mowat, A. C. Skapski, and G. Wilkinson, *Chem. Commun.*, 1477 (1971).

(41) (a) P. Friedrich, G. Besl, E. O. Fischer, and G. Huttner, *J. Organometal. Chem.*, **139**, C68 (1977); (b) E. O. Fischer, R. L. Clough, G. Besl, and F. R. Kreissl, *Angew. Chem., Int. Ed. Engl.*, **15**, 543 (1976); (c) C. P. Casey, L. D. Albin, and T. J. Burkhardt, *J. Am. Chem. Soc.*, **99**, 2533 (1977); (d) E. O. Fischer and W. Held, *J. Organometal. Chem.*, **112**, C59 (1976).

the 18-electron complex may not be a prerequisite for rearrangement. The reverse (olefin → alkylidene) is an intriguing method of generating the "first carbene" in an olefin metathesis reaction.[5b]

An obvious minimum requirement for stability is that the alkylidene ligand should not attack another ligand in the complex. For example, PR_3 ligands are compatible with nucleophilic alkylidene ligands in these species ($TaCp_2(CHCMe_3)Cl + PMe_3 \rightarrow TaCp_2(CHCMe_3)(PMe_3)^+Cl^-$) but CO is not ($TaCp_2(CHCMe_3)Cl + CO \rightarrow TaCp_2(O{=}C{=}CHCMe_3)Cl$).[14] The reverse is true for electrophilic alkylidene ligands.[29] Therefore one might expect to find many more Nb and Ta alkylidene complexes containing tertiary phosphine ligands in the future.

α-Hydrogen Abstraction from Alkyl Ligands

Let us now turn to the question of how and why these Nb and Ta alkylidene complexes form.

The steric and electronic effects which set up H_α to be abstracted from C_α in electron-deficient neopentylidene and benzylidene complexes almost certainly operate to some extent in the corresponding electron-deficient alkyl complexes which are their precursors. Since the $M{-}C_\alpha{-}C_\beta$ angle will naturally be less than the $M{=}C_\alpha{-}C_\beta$ angle (*formally* sp^3 vs. sp^2 C_α) the steric effect *may* be more important than the electronic effect. It alone could be sufficient since neopentyl α-protons are anomalously acidic even in neopentylphosphonium salts[42] where the "steric assistance"[43] is slight and evidently undetectable in the form of low values for J_{CH_α} in either phosphonium salts or the corresponding ylides.[44] We should note, however, that $M{-}C_\alpha{-}C_\beta$ angles in many bulky alkyl complexes of the early transition metals *are* abnormally large[3] (e.g., 128° in $Ta(CH_2CMe_3)_3[C(CMe_3)(Li{\cdot}dmp)]$[27b]) and $^1J_{CH_\alpha}$ is often *small* (e.g., 105 Hz in the axial CH_2CMe_3 ligand in $Ta(CH_2CMe_3)_4Cl$[12b]). Whether the latter is due only to a steric effect or whether the electrophilic metal *is* interacting with H_α in the alkyl ligand is an intriguing question. It seems plausible that in a Nb or Ta alkyl complex an α-hydrogen atom is drawn toward a "semibridging" position from which it can be more readily removed as a "proton" by another alkyl ligand. This viewpoint is consistent with our findings as follows: (i) α Abstraction from a CH_2R ligand will be much more likely in the order R = CMe_3 > Ph ≫ H (as yet unobserved). The $M{-}C_\alpha{-}R$ angle is going to be largest when R = CMe_3 and H_α consequently will be pushed and pulled most toward the position where it can be removed by another alkyl. (ii) Since a larger $M{-}C_\alpha{-}C_\beta$ angle increases the likelihood that an α-hydrogen will be removed, α abstraction would seem more likely in a crowded coordination sphere where the $M{-}C_\alpha{-}C_\beta$ angle is forced open. A coordination number of five is probably the minimum which would ensure that the molecule is crowded. α Abstraction in six- or seven-coordinate species seems equally if not more likely. (It is at present uncertain whether the two alkyl ligands must be cis to one another.) (iii) α Abstraction would be more efficient if one alkyl (the "leaving group") could be differentiated from the one from which an α hydrogen is removed. This is most obviously possible in a trigonal-bipyramidal species such as $Ta(CH_2CMe_3)_4Cl$ (1)[12b] in which one neopentyl ligand must be axial.[46] Differentiation is also possible in six- or seven-coordinate, or even square-planar species, but seems less plausible in tetrahedral species. (iv) Finally, any change in the ligands which increases the electrophilicity of the metal should increase the rate of α abstraction. [Note that α abstraction is easier in bromides (Br is a poorer π donor than Cl).] Phosphines probably *add* electron density to the metal, but apparently what is gained by making the coordination sphere more crowded outweighs this adverse electronic effect. Although an intramolecular acid/base type reaction is a useful description of α abstraction in Nb(V) and Ta(V) alkyl complexes, it is only a formalism. In general it will not be possible to accurately describe H_α as it reaches the transition state and forms a bond to the α-carbon atom of the alkyl "leaving group".

Are other metals electron-deficient enough to behave like Nb(V) and Ta(V)? Probably. It is already known that Mo and W neopentylidene and neopentylidyne complexes can be prepared by methods similar to those used to prepare Nb and Ta species.[48] Green has "trapped" the methylene hydride arising from "$Cp_2WCH_3^+$".[49] Shapley has observed a methyl ⇄ methylene hydride equilibrium in an osmium cluster.[50] It has also been known for some time that metals in 16-electron complexes will strongly interact with hydrogen atoms on nearby carbons;[51] in one instance a bridging H_α was proposed[51e] based on a $^1J_{CH_\alpha}$ coupling constant of 74 Hz.[51f] Yet an exactly analogous α-abstraction reaction may not be favorable in later transition-metal complexes. Recent studies concerning neopentyl complexes of Ru,[52] Rh,[52] and Pt[53] indicate that they decompose by apparent γ-hydrogen abstraction to give β,β-dimethylmetallocyclobutane complexes.

I thank the National Science Foundation for supporting this research and the students whose names appear in the references for their hard work and enthusiasm.

(42) (a) For example, $Ph_3P{=}CH_2$ reacts with $Ph_3PCH_2CMe_3$ to give $Ph_3P{=}CHCMe_3$;[42b] exactly the reverse would be predicted (and is observed;[42c] $Ph_3P{=}CHMe + Ph_3PMe^+ \rightarrow Ph_3P{=}CH_2$) based on electronic considerations alone. (b) D. Seyferth and G. Singh, *J. Am. Chem. Soc.*, **87**, 4156 (1965). (c) D. Seyferth, W. B. Hughes, and J. K. Heeren, *ibid.*, **87**, 2847 (1965).

(43) H. C. Brown, *J. Chem. Soc.*, 1248 (1956).

(44) $^1J_{CH_\alpha}$ in methyl- and neopentylphosphonium salts is somewhat larger the "normal"[6] (134 Hz in $[Me_4P]^+$[45a] and 140 ± 5 Hz in $[Ph_3PCH_2CMe_3]^+$[15]); $^1J_{CH_\alpha}$ in the corresponding phosphoranes is even larger (149 Hz in $Me_3P{=}CH_2$[45a,b] and 155 ± 2 Hz in $Ph_3P{=}CHCMe_3$[15]).

(45) (a) T. A. Albright, W. I. Freeman, and E. E. Schweizer, *J. Am. Chem. Soc.*, **97**, 940 (1975); (b) H. Schmidbaur, W. Richter, W. Wolf, and F. H. Kohler, *Chem. Ber.*, **108**, 2649 (1975).

(46) True five-coordinate Nb and Ta organometallics will almost certainly have structures analogous to As or Sb organometallics,[47] trigonal bipyramids with the most electronegative substituent(s) in the axial position(s). This geometry is implied by low-temperature ^1H and ^{13}C studies of $Ta(CH_2CMe_3)_4(X)$ (X = Cl[12b] or $OCMe_3$).

(47) G. O. Doak and L. D. Freedman, "Organometallic Compounds of Arsenic, Antimony, and Bismuth", Wiley-Interscience, New York, 1970.

(48) D. N. Clark and R. R. Schrock, *J. Am. Chem. Soc.*, **100**, 6774 (1978).

(49) N. J. Cooper and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 209, 761 (1974).

(50) R. B. Calvert and J. R. Shapley, *J. Am. Chem. Soc.*, **99**, 5225 (1977).

(51) (a) S. Trofimenko, *Inorg. Chem.*, **9**, 2493 (1970); (b) F. A. Cotton and V. W. Day, *J. Chem. Soc., Chem. Commun.*, 415 (1974); (c) F. A. Cotton and A. G. Stanislowski, *J. Am. Chem. Soc.*, **96**, 5074 (1974); (d) F. A. Cotton, T. LaCour, and A. G. Stanislowski, *ibid.*, **96**, 754 (1974); (e) M. Brookhart, T. H. Whitesides, and J. M. Crockett, *Inorg. Chem.*, **15**, 1550 (1976); (f) G. A. Olah, G. Liang, and S. H. Yu, *J. Org. Chem.*, **41**, 2227 (1976); (g) S. D. Ittel, F. A. Van-Catledge, C. A. Tolman, and J. P. Jesson, *J. Am. Chem. Soc.*, **100**, 1317 (1978).

(52) R. A. Andersen, R. A. Jones, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 446 (1978).

(53) G. M. Whitesides, private communication.