# Multiple Metal-Carbon Bonds. 5.[1] The Reaction of Niobium and Tantalum Neopentylidene Complexes with the Carbonyl Function

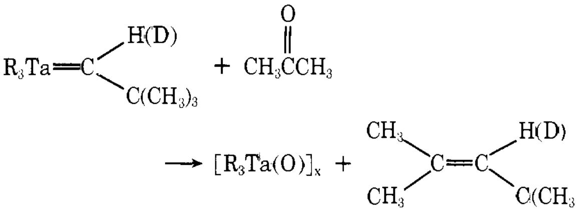
*Sir:*

Several alkylidene complexes of Nb and Ta have been reported in the recent literature.[1,2] One of these, $Ta[CH_2C(CH_3)_3]_3[CHC(CH_3)_3]$ (**1**),[1d] is a structural analogue of a phosphorus ylide while the polarity of the metal-alkylidene bond in a second, $Ta(\eta^5\text{-}C_5H_5)_2(CH_3)(CH_2)$,[1a,b] was shown to be similar to that in a phosphorus ylide; i.e., the methylene carbon atom is nucleophilic. Therefore, it was of interest to examine how such "transition metal ylides" react with the organic carbonyl function.

A 1-mmol sample of orange **1** in pentane under $N_2$ reacts instantly and exothermically at 25 °C with 1 mmol of acetone to give an ivory-colored precipitate and a nearly colorless solution. The precipitate was filtered off and all volatiles in the filtrate were bulb/bulb transferred in vacuo; only traces of nonvolatiles remained. GLC analysis showed a single major volatile product, 2,4,4-trimethyl-2-pentene, which was first identified by mass spectroscopy, then by preparative GLC isolation and comparison of its $^1H$ NMR spectrum with that of an authentic sample. The yield in three experiments varied from 75 to 85% (according to quantitative GLC analysis). The yield in $C_6D_6$ vs. an internal toluene standard was similar according to an $^1H$ NMR spectrum of the filtered solution; no other significant products were detected in this spectrum.

The precipitate from the above reaction was dried in vacuo. Its weight corresponded to that expected for a high yield of "$Ta[CH_2C(CH_3)_3]_3(O)$" (**2**). Its infrared spectrum (>600 $cm^{-1}$) in Nujol showed all the significant absorptions found in the corresponding spectrum of $Ta[CH_2C(CH_3)]_3Cl_2$ along with a strong absorption at 870 $cm^{-1}$. Since it is insoluble in common solvents, a polymeric structure with Ta-O-Ta bonds is proposed.[4] A carefully prepared sample analyzed reasonably satisfactorily (Calcd for $TaC_{15}H_{33}O$: C, 43.90; H, 8.09; O, 3.90. Found: C, 42.47; H, 7.77; O, 4.11). So far, a more tractable derivative has not been prepared.

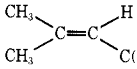
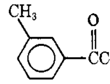
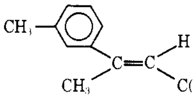
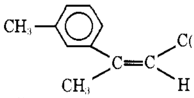
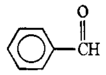
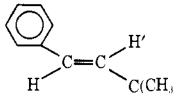
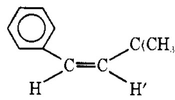
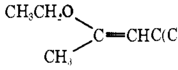
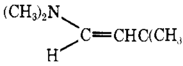
The reaction of $Ta[CH_2C(CH_3)_3]_3\{C[C(CH_3)_3][Li{\cdot}L]\}$ (L = a diamine) with $CF_3CO_2D$ gives **1**-$d_1$[1c] which, by $^1H$ NMR, was shown to be labeled at the neopentylidene $\alpha$-carbon atom to the extent of 80-90%. The reaction of a sample of **1**-$d_1$ (80 ± 5% $CDC(CH_3)_3$) with acetone gave 2,4,4-trimethyl-2-pentene, 81% of which contained D at C3 according to its mass spectrum;[5] the remainder was unlabeled. Therefore, only the neopentylidene ligand plays an active role and the overall reaction (eq 1; R = $CH_2C(CH_3)_3$) is consequently closely related to the Wittig reaction with phosphorus ylides.[6]



(1)

Red $Nb[CH_2C(CH_3)_3]_3[CHC(CH_3)_3]$ (**3**), prepared in a

Table I. Representative Reactions Using $Ta[CH_2C(CH_3)_3]_3[CHC(CH_3)_3]$[a]

| No. | Compound | Solvent | Products | Yield (method) |
|---|---|---|---|---|
| I | $CH_3C({=}O)CH_3$ | Ether or hexane |  | 80%, (GLC)[b,c] |
| II |  | Hexane |  (35%)[d]<br> (65%)[d] | 90% (isolated[e]) |
| III |  | Pentane |  (35%)[b]<br> (65%)[b] | 90% (isolated[e])[f] |
| IV | $CH_3CH_2OC({=}O)CH_3$ | Ether, pentane, or $C_6D_6$ | <br>(2:1 isomeric mixture)[b] | 60% ($^1H$ NMR[g]) |
| V | $(CH_3)_2NC({=}O)H$ | Ether, pentane, or $C_6D_6$ | <br>(~95% one isomer)[h] | 77% ($^1H$ NMR[g]) |
| VI | $CH_3CH_2OC({=}O)H$ | $C_6D_6$ | $CH_3CH_2OCH{=}CH'C(CH_3)_3$<br>(50% cis, 50% trans) | 90% ($^1H$ NMR[g])[i] |

[a] Reactions were run on a 1–2 mmol scale using pure, isolated $Ta[CH_2C(CH_3)_3]_3[CHC(CH_3)_3]$. 2,4,4-Trimethyl-2-pentene was identified by $^1H$ NMR comparison with an authentic sample while the others were identified by a combination of $^1H$ NMR and mass spectroscopy. The $^1H$ NMR spectra of *cis*- and *trans-tert*-butylstyrene-$d_0$ and -$d_1$ compared well with the spectra of *cis*- and *trans*-propenylbenzene, respectively.[f] Other isomer proposals are based on estimated chemical shifts of olefinic protons and coupling constants (see R. M. Silverstein, G. C. Bassler, and T. C. Merrill, "Spectrometric Identification of Organic Compounds", Wiley, New York, N.Y., 1974, appendices e and f). [b] Isolated by preparative gas chromatography. [c] Benzophenone and cyclohexanone gave ca. 80% yields of the expected olefins by $^1H$ NMR[g] and mass spectroscopy. [d] $J_{CH_3H_t} \approx J_{CH_3H_c} = 1\text{–}2$ Hz; $\tau_{H_t}$ 4.29, $\tau_{H_c}$ 4.58 in $CDCl_3$. [e] Solvent was removed in vacuo. [f] In trans olefin, $\tau_H = \tau_{H'} = 3.72$; in cis olefin, $\tau_H$ 3.57, $\tau_{H'}$ 4.40, $J_{HH'} = 12.5$ Hz; (solvent = $CDCl_3$; cf. *cis*-propenylbenzene in $CCl_4$ where $\tau_H$ 3.68 and $\tau_{H'}$ 4.39; $J_{HH'} = 10.5$ Hz). A reaction using $Ta[CD_2C(CH_3)_3]_3[CDC(CH_3)_3]$ gave an olefin mixture whose $^1H$ NMR spectrum showed two broad singlets at $\tau$ 3.57 (area ≈ 2) and $\tau$ 3.72 (area ≈ 1). [g] Reactions were done in $C_6D_6$ with an internal toluene standard. [h] Olefin protons at $\tau$ 4.18 and $\tau$ 5.70 in $C_6D_6$; $J_{HH} \approx 13$ Hz suggests trans isomer. [i] $\tau_{H_t}$ 3.82, $\tau_{H_t'}$ 5.17, $J_{H_tH_t'} = 13$ Hz; $\tau_{H_c}$ 4.47; $\tau_{H_c'}$ 5.78; $J_{H_cH_c'} = 7$ Hz; solvent = $C_6D_6$.

manner analogous to **1**,[7] also reacts with acetone in pentane to give high yields of 2,4,4-trimethyl-2-pentene and an insoluble, ivory-colored precipitate whose infrared spectrum in Nujol is essentially identical with that of **2** ($\nu_{Nb-O}$ 880 cm$^{-1}$). Since obtaining large quantities of **3** is more difficult, however, **1** was used in further studies.

Table I lists some representative reactions of **1** with other common molecules containing the carbonyl function. Most were done on a 1-2 mmol scale with isolated **1** at 25° in the solvents shown. Alternatively **1** can be prepared in situ in pentane in quantitative yield from $Ta[CH_2C(CH_3)_3]_3Cl_2$ and 2 mol of $LiCH_2C(CH_3)_3$.[8] It can also be prepared directly from $TaCl_5$ and 5 mol of $(CH_3)_3CCH_2MgCl$ in diethyl ether but the reaction to give **1** is slow and the yield of olefin consequently suffers.[9]

Most notable of the Wittig-type reactions employing **1** are those which are not (or very rarely) successful with phosphorus ylides, IV-VI. **1** also reacts instantly with $CO_2$ to give at least a 50% yield (vs. theory) of di-*tert*-butylallene according to GLC/mass spectral analysis and $^1$H NMR ($\tau$ 4.8 (1), $\tau$ 8.9 (9) in $C_6D_6$). In general, esters and amides appear to react more slowly than ketones and aldehydes, and molecules which are more substituted at the carbonyl carbon more slowly than those which have a more exposed carbonyl function (e.g., ethyl acetate reacts more slowly than ethyl formate). Molecules with bulky substituents (e.g., pivaldehyde) react too slowly under these conditions for practical purposes. Though relative rates of reaction and solvent effects have not been studied thoroughly, one could envision some degree of selectivity between isolated functional groups. It should also be noted in this context that **1** (in pentane) does not react readily with $CH_3I$, $C_6H_5CH_2Cl$, or ethylene oxide.

The overall reaction of the type shown in eq 1 formally consists of addition of the carbonyl function across the $Ta{=}CHCMe_3$ bond in a manner consistent with a $Ta(\delta+){=}C(\delta-)$ polarization. This is evidence that the neopentylidene $\alpha$-carbon atom in **1**, like the methylene carbon atom in $Ta(\eta^5\text{-}C_5H_5)_2(CH_3)(CH_2)$,[1b] is nucleophilic. Note that carbene complexes in which $C_{carb}$ is electrophilic react in the expected, opposite manner with polarized "unsaturated" bonds as in (for example) a phosphorus ylide.[10]

The mechanism of the reaction of **1** with the carbonyl function probably consists of at least two distinct steps. For example, when ethyl acetate is added to **1** in ether, the orange color changes hue slightly and heat is evolved. Shortly thereafter the color lightens steadily as **2** precipitates from the solution. Since **1** is electron deficient (14 valence electrons), and ketones and aldehydes are known to bond through the carbonyl oxygen atom to the metal in other electron-deficient Ta or Nb alkyls such as $Nb(CH_3)_2Cl_3$,[11] the first step in the reaction of **1** with a carbonyl function may simply be formation of a similar adduct. Subsequent "metathesis" then yields the olefin and oxygen strongly bound to Ta (initially probably $Ta{=}O$). Some support for this proposal comes from the observation that $Ta(\eta^5\text{-}C_5H_5)_2(CH_3)(CH_2)$, an 18-electron complex, only reluctantly reacts with acetone (80° in neat acetone) to give low yields of isobutylene. A betaine intermediate analogous to that invoked as an intermediate in the Wittig reaction[6] of course cannot be excluded by any of these data alone.

The findings reported here demonstrate that **1** is indeed a powerful, if somewhat esoteric, reagent for the preparation of *tert*-butyl substituted olefins, not only from aldehydes and ketones, but from esters and amides; several would probably prove difficult to prepare by standard techniques due to the steric demands of the *tert*-butyl substituent. They also demonstrate that analogies between early transition metals and main group elements can be significant and useful, and that some metal carbene complexes (at least $Ta(\eta^5\text{-}C_5H_5)_2(CH_3)(CH_2)$[1a,b] and possibly also **1**) can be described more accurately in terms of the ylide-type structure, $M(\delta+){=}C(\delta-)$.

**Acknowledgment.** The author wishes to thank Professor Grant Urry of Tufts University for valuable discussions concerning the reaction of **1** with aldehydes and ketones.

## References and Notes

(1) (a) Part **4**, L. J. Guggenberger and R. R. Schrock, *J. Am. Chem. Soc.*, **97**, 6578 (1975); (b) 3, R. R. Schrock, *ibid.*, **97**, 6577 (1975); (c) 2, L. J. Guggenberger and R. R. Schrock, *ibid.*, **97**, 2935 (1975); (d) 1, R. R. Schrock, *ibid.*, **96**, 6796 (1974).

(2) "Alkylidene" complex is the preferred, more succinct description of what might also be called an "unstabilized carbene" complex. ("Stabilized carbene" complexes generally are those which contain a heteroatom such as O or N bound to the carbene carbon atom; see, for example, D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, **72**, 545 (1972), and references therein.) "Terminal" alkylidene complexes (i.e., $M{=}CHR$, R = alkyl or aryl) are so far unique to Nb and Ta though diphenylmethylene complexes of W[3a] and Mn,[3b] a benzocyclobutenylidene complex of Fe,[3c] and a diphenylcyclopropylidene complex of Cr[3d] are known.

(3) (a) C. P. Casey and T. J. Burkhardt, *J. Am. Chem. Soc.*, **95**, 5833 (1973); (b) W. A. Herrman, *Chem. Ber.*, **108**, 486 (1975); (c) A. Sanders, L. Cohen, W. Giering, D. Kenedy, and C. V. Magatti, *J. Am. Chem. Soc.*, **95**, 5430 (1973); (d) K. Öfele, *Angew. Chem., Int. Ed. Engl.*, **7**, 950 (1968).

(4) (a) The oxyhalides, $Nb(O)Cl_3$ and $Ta(O)Cl_3$, are also polymers in the solid state ($\nu_{M-O} \approx 770$ cm$^{-1}$)[4b,c] but monomers in the gas phase ($\nu_{M=O} \approx 1000$ cm$^{-1}$)[4b,c] while $V(O)Cl_3$ ($\nu_{V=O}$ 1035 cm$^{-1}$)[4b,c] and $V(O)[CH_2Si(CH_3)_3]_3$ ($\nu_{V=O}$ 990 cm$^{-1}$)[4d] are monomers in the solid state. Therefore a polymeric Ta–O–Ta formulation for **2** ($\nu_{Ta-O}$ 870 cm$^{-1}$) is not unreasonable though a lower value for $\nu$ might have been expected based on the above data. (b) D. L. Kepert, "The Early Transition Metals", Academic Press, New York, N.Y., 1972; (c) R. A. Walton, *Prog. Inorg. Chem.*, **16**, 1 (1972); (d) W. Mowat, A. Shortland, G. Yaqupsky, N. J. Hill, M. Yaqupsky, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 533 (1972).

(5) Detailed mass spectral analysis courtesy of F. J. Kitson of the Central Research and Development Department.

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

(7) **3** is the product of the reaction between $Nb[CH_2C(CH_3)_3]_3Cl_2$ and 2 mol of $LiCH_2C(CH_3)_3$ in pentane at −78°. It is a red crystalline solid which is extremely soluble in pentane and (unlike **1**) does not sublime without decomposing. Its $^1$H and $^{13}$C NMR spectra are essentially identical with **1** and its identity thereby established. (Its thermal instability hampered meaningful elemental analyses.)

(8) $Ta[CH_2C(CH_3)_3]_3Cl_2$ is best prepared by stirring 1.5 mol of $Zn[CH_2C(CH_3)_3]_2$ and $TaCl_5$ in pentane at 25 °C for 12 h (cf. S. Moorhouse and G. Wilkinson, *J. Organomet. Chem.*, **52**, C5 (1973); *J. Chem. Soc., Dalton Trans.*, 2187 (1974); W. Mowat and G. Wilkinson, *ibid.*, 1120 (1973)). $Zn[CH_2C(CH_3)_3]_2$ was prepared by the standard Grignard method (bp 82°, 27 mm).

(9) An ether solution of $(CH_3)_3CCH_2MgCl$ (50 mmol) was added to $TaCl_5$ (3.58 g, 10 mmol) in 100 ml of ether at −78 °C under $N_2$. The mixture was heated to reflux for 16 h (**1** is stable under these conditions). Addition of 3 mmol of benzaldehyde followed by hydrolysis with 1 N HCl gave an ether layer which contained a 30% yield (vs. Ta) of *cis*- and *trans*-*tert*-butylstyrene (by quantitative GLC). The major product was neopentylphenyl carbinol (ca. 2 mol per Ta). The yield of the olefin decreased to ca. 5% when the reflux step was omitted.

(10) C. P. Casey and T. J. Burkhardt, *J. Am. Chem. Soc.*, **94**, 6543 (1972).

(11) J. D. Wilkins, *J. Organomet. Chem.*, **80**, 357 (1974).

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## Transition Metal Catalyzed Asymmetric Organic Syntheses via Polymer Bound Chiral Ligands. Synthesis of *R* Amino Acids and Hydratropic Acid by Hydrogenation

*Sir:*

Although there are a number of methods for the synthesis of optically active organic compounds, there are several obvious advantages in obtaining a chiral product from a prochiral substrate via an optically active catalyst or enzyme. The reactions, via a homogeneous catalyst that owes its chirality to asymmetric phosphine ligands on the metal, have proven to be