Multiple Metal-Carbon Bonds. 6.[1] The Reaction of Niobium and Tantalum Neopentylidene Complexes with Simple Olefins: a Route to Metallocyclopentanes

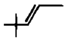
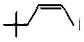
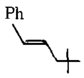
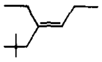
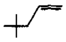
Sir:

Primary alkylidene complexes[2] have been postulated as active intermediates in several important transition metal catalyzed reactions such as olefin metathesis,[3] rearrangement of strained hydrocarbons,[4] and formation of cyclopropanes from diazoalkanes and olefins.[5] However, only Nb and Ta primary alkylidene complexes have so far been isolated and characterized. These are proving to be invaluable in probing the question of how *nucleophilic*[6] alkylidenes react with typical functional groups. We wish to report here that nucleophilic nonpentylidene complexes of Nb and Ta react rapidly with primary olefins to give a new olefin formed by rearrangement of a postulated intermediate metallocyclo*butane* complex. The isolable metal-containing product in several instances is a metallocyclo*pentane* complex formed by cycloaddition of two olefins to the metal-containing fragment which remains.

The reaction between $M(CH_2CMe_3)_2Cl_3$[8a] (M = Nb or Ta) and TlC_5H_5 at 25 °C in toluene gives neopentane and $M(\eta^5\text{-}C_5H_5)Cl_2(CHCMe_3)$[8b] (**1**, M = Ta; **2**, M = Nb). The intermediate, presumably $M(\eta^5\text{-}C_5H_5)Cl_2(CH_2CMe_3)_2$, evidently "decomposes" by α-hydrogen atom abstraction.[7] The residue obtained after filtering off TlCl was recrystallized from pentane/toluene (5:1) at −40 °C to give **1** in 70% yield (Calcd for $TaC_{10}H_{15}Cl_2$: C, 31.03; H, 3.90; Cl, 18.32. Found: C, 31.17; H, 4.05; Cl, 18.30; Bernhardt), or **2** in 15% yield (Calcd for $NbC_{10}H_{15}Cl_2$: C, 40.17; H, 5.05; Cl, 23.71. Found: C, 40.19; H, 5.16; Cl, 23.66; Bernhardt). The ^1H and ^{13}C NMR spectra for **1** and **2** are entirely consistent with formulation as neopentylidene complexes.[9] A molecular weight measurement suggests **1** is a monomer in benzene.[10] **1** is thermally stable (unchanged after 3 h at 150 °C in benzene in a sealed tube or sublimation at 1 μm and 65 °C), but reacts readily with moist air. As in other tantalum alkylidene complexes[6] the neopentylidene α-carbon atom is believed to be nucleophilic, e.g., **1** reacts with HCl at −78 °C in toluene to give $Ta(\eta^5\text{-}C_5H_5)Cl_3(CH_2CMe_3)$ in 95% isolated yield.[11] Alkylidene complexes of this type are important in two respects: (i) the 14 valence electron count should in theory allow an incoming ligand to coordinate to the metal; and (ii) the only obviously reactive, or at least potentially the most reactive ligand, is the neopentylidene ligand.

Ethylene (45 psi) reacts readily with **1** dissolved in pentane at 25 °C. The red color first deepens then lightens to yellow-orange in 3-5 min as orange crystals fall from solution (vide infra). The organic product of this reaction is almost exclusively 4,4-dimethyl-1-pentene (Table I). The yield of 3,3-dimethyl-1-butene, the metathesis product, is insignificant and the yield of *tert*-butylcyclopropane must be ≤5%. The major organic product of the reaction of **1** with propylene, styrene, and *cis*-3-hexene results from an analogous but *selective* "insertion" of neopentylidene into an olefinic C–H bond (cf. propylene and styrene). A qualitative comparison suggests that the rate of reaction of these four olefins with **1** decreases in the order ethylene > propylene ≥ styrene ≫ *cis*-3-hexene. The fact that β,β-dimethylstyrene did not react appreciably under conditions where *cis*-3-hexene was consumed is consistent with this general trend.[12] The reaction of **2** with ethylene also gives 4,4-dimethyl-1-pentene, but in lower yield.

Table I. Products of the Reaction of **1** and **2** with Olefins[a]

Compd	Olefin	Products
1	$CH_2{=}CH_2$ (45 psi)	 $(91 \pm 3\%)^{b,c}$  $(\sim3\%)^{c}$  $(\sim0\%)^{c}$  $(\leqslant0.04\%)^{c}$
1	$CH_3CH{=}CH_2$ (45 psi)	 $(86 \pm 6\%)^{b,c}$
1	$PhCH{=}CH_2$ (3 mol in C_6D_6)	 $(95 \pm 10\%)^{d,e}$
1	*cis*-3-Hexene (neat, 120 °C)	 (or isomers; > 50%)[f]
2	$CH_2{=}CH_2$ (45 psi)	 $(62 \pm 3\%)^{b,c}$

[a] Solvent = mesitylene, pentane, or C_6D_6; T = 25 °C unless otherwise noted. Minor product yields were measured only for the first example. [b] Identified by GLC and ^1H NMR comparison (in C_6D_6) with an authentic sample. [c] GLC yield based on internal standard (a saturated hydrocarbon). [d] Proposal based on ^1H NMR comparison (in C_6D_6) with the spectrum of *trans*-propenylbenzene. [e] Yield determined in C_6D_6 by ^1H NMR vs. internal cyclohexane standard. [f] The mass and ^1H NMR spectra are consistent with the major olefin product being one of this type.

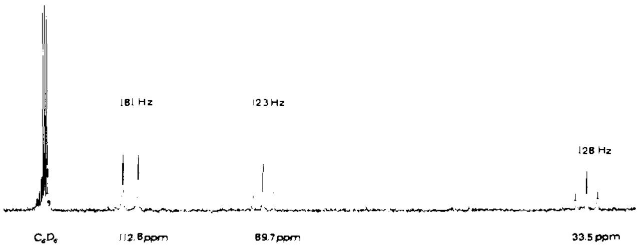
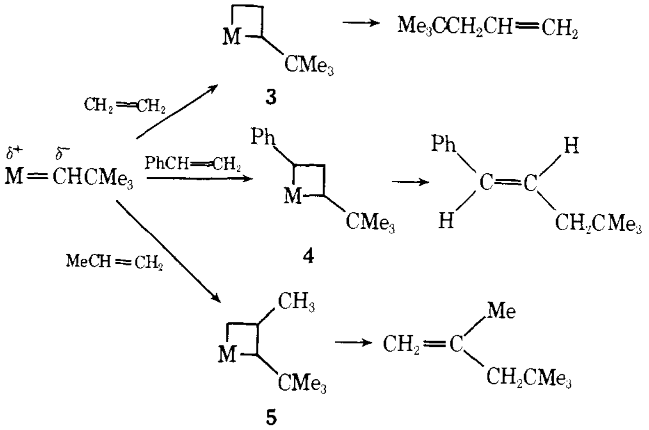


Figure 1. The 67.89-MHz gated decoupled ^{13}C spectrum of **6** in C_6D_6 at 25 °C.

Scheme I. Proposed Metallocyclobutane Intermediates



We believe that the olefin adds to the metal-neopentylidene double bond to give one metallocyclobutane intermediate[13] selectively (e.g., **3**, **4**, and **5**, Scheme I), the one which is consistent with the neopentylidene ligand's nucleophilic properties.[14] A specific hydrogen atom shift from C_β to the *tert*-butyl-substituted C_α in **3**, **4**, and **5** is one means of generating the observed product.[15] Note that (i) the same factors which determine how the olefin adds to the neopentylidene ligand[14] apparently govern the way in which an olefin adds to a postulated tungsten alkylidene complex in one type of olefin metathesis system;[16] and (ii) the rearrangement observed here is the third most obvious fate of a metallocyclobutane complex. The only other example of a reaction between an alkylidene complex $[(CO)_5W{=}C(C_6H_4R)_2$, R = H or $CH_3]$ and various nonfunctionalized olefins gave metathesis and cyclopropane products;[12b,17] no olefin products resulting from rearrangement of the intermediate metallocyclobutane complex were reported.[18]

The organometallic product of the reaction of **1** with ethylene (vide supra) can be isolated in 95% yield; it has the empirical formula $TaC_9H_{13}Cl_2$ (Calcd for $Ta_9H_{13}Cl_2$: C, 28.98; H, 3.51; Cl, 19.01. Found: C, 29.03; H, 3.63; Cl, 19.17; Bernhardt). Yellow-orange crystals of **6** darken under nitrogen in one day at 25 °C (more slowly under 600 mm of C_2H_4), but keep indefinitely at −30 °C.

The −40 °C 60-MHz ^1H NMR spectrum of **6** in toluene-d_8 under 1 atm of ethylene shows a η^5-C_5H_5 resonance at τ 4.60, a small peak for free, dissolved ethylene at τ 4.75, and two broad peaks (ca. 20-Hz wide) and two sharper peaks (ca. 10-Hz wide) at τ 6.35, 7.15, 7.95, and 8.10, respectively, of approximately equal area, and a total area of eight protons vs. η^5-C_5H_5. On warming to 40 °C, the broad pair coalesces with the sharper pair to give *two* peaks at τ 7.25 and 7.60; the peak for free ethylene remains sharp and does not shift appreciably.

The 67.89-MHz gated decoupled ^{13}C spectrum of **6** in C_6D_6 at 25 °C is shown in Figure 1. The two triplet resonances are separated by about 60 ppm. This result seems inconsistent with their being due to two types of ethylene carbon atoms, since *all* known chemical shifts for ethylene carbon atoms in widely differing neutral complexes lie in the range 20–60 ppm downfield of Me_4Si.[19] Secondly, the $^1J_{CH}$ coupling constants for the two types of carbon atoms are those expected for sp^3 hybridized carbon atoms, not coordinated ethylene.[20] Together, these facts suggest that *ground state* **6** is actually a metallocyclopentane complex. Accordingly, **6** reacts with Br_2 in diethyl ether at −78 °C to give 1,4-dibromobutane (0.83 per Ta)[24] and 1,4-dibromoethane (0.18 per Ta),[24] and with CO (3 atm) in diethyl ether at −78 °C (followed by warming to 25 °C) to give cyclopentanone (0.50 per Ta)[24] and nearly insoluble $TaCp(\eta^x\text{-}C_5H_5)Cl_2(CO)_2$[8b] (0.55 per Ta; ν_{CO} (cm^{-1}) = 2045 s, 1962 s). These results unambiguously demonstrate that a metallocyclopentane complex can be formed from two simple olefins.[25] The variable temperature ^1H NMR results noted above, however, need not be ascribed to the reverse of that process (followed by rotation of each ethylene about the metal–ethylene bond axis),[29] since pseudo-rotation in "five-coordinate" $Cl_2(\eta^5\text{-}C_5H_5)\overline{TaCH_2CH_2CH_2CH_2}$ would yield a result indistinguishable by ^1H NMR.

The organometallic product (**7**) of the reaction of **1** with propylene at 0 °C is also an isolable metallocycle analogous to **6**. Full details of the stereochemistry, variable temperature ^1H and ^{13}C NMR spectra, and role in catalytic processes of **7**, **6**, and other isolable metallocycles prepared from olefins will be reported separately.

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References and Notes

(1) Part 5. R. R. Schrock, *J. Am. Chem. Soc.*, **98,** 5399 (1976).

(2) Alkylidene complexes are defined as "carbene" complexes which contain no heteroatoms such as O, N, or S. Primary alkylidenes are monosubstituted and secondary alkylidene disubstituted methylene complexes.

(3) (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).

(4) K. C. Bishop III, *Chem. Rev.*, **76,** 461 (1976).

(5) W. Kirmse, "Carbene Chemistry", Vol. 1, Academic Press, New York and London, 1971.

(6) Nucleophilicity has been unambiguously demonstrated in one case[7] and is implied by reactions in others.[1]

(7) R. R. Schrock, *J. Am. Chem. Soc.*, **97,** 6577 (1975).

(8) (a) $Ta(CH_2CMe_3)_2Cl_3$, a yellow-orange liquid at 25 °C, can be prepared by slowly adding $Zn(CH_2CMe_3)_2$ to $TaCl_5$ (5% excess) in toluene at 25 °C. It may be used in situ or isolated by removing toluene in vacuo and recrystallizing it from pentane at −40 °C [^1H NMR (τ, C_6D_6): 7.08 (s, CH_2), 8.88 (s, CMe_3)]. Orange $Nb(CH_2CMe_3)_2Cl_3$ (also a liquid at 25 °C) can be prepared by slowly adding $Zn(CH_2CMe_3)_2$ to *2* mol of sublimed $NbCl_5$ in pentane. It decomposes readily in concentrated solutions (toluene or pentane) at 25 °C [^1H NMR (τ, C_6H_6): 6.20 (br s, CH_2); 8.80 (s, CMe_3)]. (b) Until proven otherwise, we will assume that all complexes contain η^5-C_5H_5. In only one example so far, $Ta(C_5H_5)Cl_2(CO)_2$ (see text), does infrared evidence suggest that an η^1-C_5H_5 formulation in the solid state may be more correct.

(9) (a) **1:** 60-MHz ^1H NMR (τ, C_6D_6) 3.62 (s, 1, =CH–), 4.35 (s, 5, η^5-C_5H_5), 9.05 (s, 9, CMe_3); 22.63-MHz ^{13}C NMR (ppm downfield from Me_4Si, C_6D_6, gated decoupled) 246 (d, C_α, $^1J_{CH}$ = 84 Hz), 107 (d, η^5-C_5H_5, $^1J_{CH}$ = 180 Hz), 48 (s, C_β), 33 (q, C_γ, $^1J_{CH}$ = 126 Hz). (b) **2:** 60-MHz ^1H NMR (τ, C_6D_6) 2.75 (s, 1, =CH–), 4.20 (s, 5, η^5-C_5H_5), 9.05 (s, 9, CMe_3).

(10) Only one measurement was made: calcd 388; found 494. The high result may indicate some dimerization through chlorine atoms.

(11) This complex can be prepared by reacting $Ta(CH_2CMe_3)Cl_4$ [from excess $TaCl_5$ and $Zn(CH_2CMe_3)_2$ in toluene after 3 days: ^1H NMR (τ, C_6D_6) 6.58 (s, 2, CH_2), 8.98 (s, 9, CMe_3)] with TlC_5H_5 in toluene at 25 °C [^1H NMR (τ, C_6D_6) 4.34 (s, 5, C_5H_5), 8.12 (s, 2, CH_2), 8.61 (s, 9, CMe_3)].

(12) (a) Casey[12b] found a similar relative reactivity of nonfunctionalized olefins with $W(CO)_5(Ctol_2)$ [tol = *p*-$C_6H_4CH_3$]. Steric factors alone could be largely responsible for the observed trend in each case. (b) C. P. Casey, H. E. Tuinstra, and M. C. Saeman, *J. Am. Chem. Soc.*, **98,** 608 (1976).

(13) (a) So far, we have not found conditions which would allow us to isolate and characterize these complexes. Stable metallocyclobutane complexes are known for Pt[13b] and W.[13c,d] Note that decomposition of each in the solid state gives some of the olefin expected by a process analogous to that described here. Brown[13e] has also noted that cyclopropane reacts with $[Pt(C_2H_4(Cl_2]_2$ to give $[Pt(propylene)Cl_2]_2$ in CH_2Cl_2. (b) P. W. Hall, R. J. Puddephatt, and C. F. H. Tipper, *J. Organomet. Chem.*, **84,** 407 (1975), and references cited therein; (c) M. Ephritikhine, M. L. H. Green, and R. E. MacKenzie, *J. Chem. Soc., Chem. Commun.*, 619 (1976); (d) M. Ephritikhine and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 926 (1976); (e) D. B. Brown, *J. Organomet. Chem.*, **24,** 787 (1970).

(14) Of course we do not yet know exactly how the proposed metallocyclobutane complex forms, but an important consideration must be a polarization (almost certainly in a transition state) which places some positive charge on the metal and some negative charge on one olefinic carbon atom (e.g., the carbon next to the phenyl group in the case of styrene and the unsubstituted carbon in the case of propylene) as a single bond forms between the neopentylidene α-carbon atom and the second olefinic carbon atom.

(15) If this process proceeds via a σ- or π-allyl hydride complex, then it is a form of β-hydride elimination. An intriguing possibility which cannot be excluded, however, is a form of α-hydrogen atom abstraction[7] to give a new alkylidene complex (e.g., $M{=}CHCH_2CH_2CMe_3$ in the case of ethylene) followed by a now possibly more facile β-hydride shift to the alkylidene α-carbon atom.

(16) P. G. Gassman and T. H. Johnson, *J. Am. Chem. Soc.*, **99,** 622 (1977).

(17) (a) Note that C_α in $(CO)_5W{=}CPh_2$ is believed to be electrophilic. (b) C. P. Casey and T. J. Burkhardt, *J. Am. Chem. Soc.*, **96,** 7808 (1974); (c) C. P. Casey, T. J. Burkhardt, C. A. Bunnell, and J. C. Calabrese, *ibid.*, in press.

(18) Since the observed products do not account for all the alkylidene initially present, such products might still be found in the reaction mixtures.

(19) (a) Chemical shifts are known for five neutral compounds: $(PPh_3)_2Pt(C_2H_4)$, 39.6;[19b] $(\eta^5\text{-}C_5H_5)Rh(C_2H_4)_2$, 60.2;[22] $(acac)Rh(C_2H_4)_2$, 36.3;[22] $NbH(C_2H_4)_2(dmpe)_2$, 32 and 35;[19c] and $Ta(\eta^5\text{-}C_5H_5)_2(CH_3)(C_2H_4)$, 19.8 and 20.5.[23] (b) M. H. Chisholm and S. Godleski, *Prog. Inorg. Chem.*, **20,** 299 (1976); (c) R. R. Schrock, *J. Organomet. Chem.*, **121,** 373 (1976).

(20) The $^1J_{C_\alpha H}$ coupling constant in *all* tantalum methyl and benzyl complexes in hand lie in the range expected[21] for sp^3 hybridized carbon atoms, 125 ± 3 Hz. In contrast, the CH coupling constant in free ethylene[21] is 156 Hz and in ethylene in $Rh(\eta^5\text{-}C_5H_5)(C_2H_4)_2$[22] is 160 Hz, while in $Ta(\eta^5\text{-}C_5H_5)_2(C_2H_4)(CH_3)$[23] it is 150 Hz.

(21) D. M. Graham and C. E. Holloway, *Can. J. Chem.*, **41,** 2114 (1963).

(22) G. M. Bodner, B. N. Storhoff, D. Doddrell, and L. J. Todd, *Chem. Commun.*, 1530 (1970).

(23) C. D. Wood and R. R. Schrock, unpublished results.

(24) By GLC vs. an internal standard.

(25) Unsubstituted metallocyclopentane complexes have been prepared by reacting 1,4-dilithiobutane with metal dihalides.[26,27] Formation of well-characterized metallocyclopentane complexes only from more reactive olefins like norbornadiene has been observed in the past.[26] Results in one report,[26] however, could be interpreted as evidence for formation of a metallocyclopentane complex from ethylene.

(26) J. X. McDermott, M. E. Wilson, and G. M. Whitesides, *J. Am. Chem. Soc.*, **98,** 6529 (1976).

(27) (a) G. Biefeld, H. A. Eick, and R. H. Grubbs, *Inorg. Chem.*, **12,** 2166 (1973); (b) R. H. Grubbs, D. C. Carr, and P. L. Burk in "Organotransition Metal Chemistry", Y. Ishii and M. Tsutsui, Ed., Plenum Press, New York, N.Y., 1975.

(28) A. R. Fraser, P. H. Bird, S. A. Bezman, J. R. Shapley, R. White, and J. A. Osborn, *J. Am. Chem. Soc.*, **95,** 597 (1973).

(29) See R. Cramer, J. B. Kline, and J. D. Roberts [*J. Am. Chem. Soc.*, **91,** 2519 (1969)] for a Rh example, $Rh(\eta^5\text{-}C_5H_5)(C_2H_4)_2$.

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