reactions in which the stronger coupling between reactant centers can lead to a stronger dependence on the donor–acceptor energy gap.

In the extreme free-energy region ($-\Delta G_{ab}^\circ > 4[\Delta G_{i,ab}^\ddagger - w]$), most available evidence suggests that α approaches zero. However, quantum mechanical models,[7,8a] in which the relaxation from reactant pair to product pair is treated as an isoenergetic tunneling process, predict some variation of α in this region. In most of the systems investigated to date for which $|\Delta G_{ab}^\circ| > 4(\Delta G_{i,ab}^\ddagger - w)$, $\Delta X \approx 0$, and the potential energy surfaces of reactant and product pairs are distinguishable only owing to the nearly classical motions of the surrounding solvent molecules. It seems unlikely that the resulting reactant and product potential energy surfaces would be sufficiently well-defined that quantum constraints on the transition are meaningful. In this regard, investigation of the highly exoergic region of systems in which ΔX is reasonably large would be very useful.

Conclusions

The axial bond lengths in low-spin $Co(N_4)(OH_2)_2^{2+}$ complexes are tens of picometer longer than the $Co-OH_2$ bond lengths in cobalt(III) complexes. Rate variations of outer-sphere (self-exchange) electron-transfer reactions of the $Co(N_4)(OH_2)_2^{3+,2+}$ couples are largely dictated by the resulting differences in first coordination sphere reorganizational barriers. These rate variations are in accord with either quantum or classical mechanical descriptions of the Franck–Condon barrier. Comparisons with the self-exchange rate of the $Ru(bpy)_2(NH_3)_2^{3+,2+}$ couple suggest that the $Co(N_4)(OH_2)_2^{3+,2+}$ self-exchange reactions are "nonadiabatic" with $\kappa_{el} \approx 10^{-3\pm1}$. The free-energy dependence of the reaction rates for oxidations of $Co(N_4)(OH_2)_2^{2+}$ and reductions of $Co(N_4)(OH_2)_2^{3+}$ complexes is adequately described by the classical expressions obtained by Marcus.

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Supplementary Material Available: Tables of atomic parameters, of kinetic parameters, and of force constants and bond lengths (18 pages). Ordering information is given on any current masthead page.

How Niobium and Tantalum Complexes of the Type $M(CHCMe_3)(PR_3)_2Cl_3$ Can Be Modified To Give Olefin Metathesis Catalysts[1]

S. M. Rocklage, J. D. Fellmann, G. A. Rupprecht, L. W. Messerle, and R. R. Schrock*

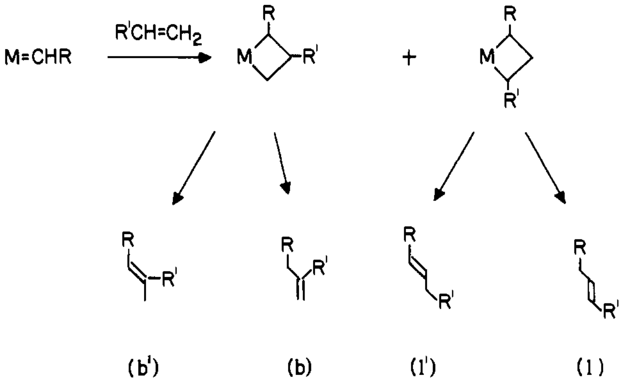
Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received July 14, 1980*

Abstract: Complexes of the type $M(CHR)L_2X_3$ (M = Nb or Ta, R = CMe_3 or Ph, L ≘ a tertiary phosphine, X = Cl or Br) react with terminal olefins to give the organic products of β-hydride rearrangement of the four possible intermediate metallacyclobutane complexes. We see no metathesis products or cyclopropanes. When L = THF or py, the complex reacts with ethylene to give ~10% metathesis product, with 1-butene to give ~50% metathesis products, and with *cis*-2-pentene to give exclusively metathesis products. $Ta(CHCMe_3)(THF)_2Cl_3$ is a short-lived metathesis catalyst for *cis*-2-pentene. Complexes of the type $M(CHCMe_3)(OCMe_3)_2Cl(PMe_3)$ react with terminal and internal olefins to give only metathesis products and are longer lived (ca. 35 turnovers) metathesis catalysts for *cis*-2-pentene. The major chain termination steps in metathesis of a terminal olefin are decomposition (probably intermolecular) of intermediate methylene complexes and rearrangement of intermediate metallacyclobutane complexes. The major chain termination step in metathesis of *cis*-2-pentene is rearrangement of an alkylidene ligand in an intermediate alkylidene complex to an olefin.

Introduction

The reaction between an alkylidene complex and an olefin is the favorite proposed mechanism for scrambling alkylidene fragments in the olefin metathesis reaction.[2] Therefore we have been interested for some time in how niobium- and tantalum-alkylidene complexes[3] react with olefins. The first type which contained no other potentially reactive ligands which might complicate such studies was $Ta(\eta^5-C_5H_5)(CHCMe_3)Cl_2$.[4] It reacts with terminal olefins to give a tantallacyclobutane complex which rapidly rearranges to an unobservable olefin complex by migration of a β-proton to an α-carbon atom. Two equivalents of the smaller, more strongly coordinating olefin which is present in excess then displaces this new olefin to give a tantallacyclo-

Scheme I. The Four Products Formed on Reacting a Halo/Alkylidene Complex with a Terminal Olefin (See Table I)



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[1] Multiple Metal-Carbon Bonds. 19. For part 18 see: Fellmann, J. D.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 6608.

[2] (a) Calderon, N.; Lawrence, J. P.; Ofstead, E. A. *Adv. Organomet. Chem.* **1979**, *17*, 449–492 and references therein. (b) Grubbs, R. H. *Prog. Inorg. Chem.* **1978**, *24*, 1–50.

[3] Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98–104.

[4] Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210–3222.

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Table I. Organic Products of Reactions between Halophosphine Complexes and Olefins[a]

		products[b]				
M=CHR complexes	olefin (R'CH=CH$_2$)	b	b'	l	l'	other
Ta(CHPh)(PMe$_3$)$_2$Cl$_3$	ethylene			73	27	*c*
(R = Ph)	propylene	49	21	4	26	*d*
	styrene	5	49	46		*e*
Ta(CHCMe$_3$)(PMe$_3$)$_2$Cl$_3$	ethylene[f]			7	93	
(R = CMe$_3$)	propylene[g]	8	42	7	43	
	styrene	6	35	30	29	

[a] Yields shown here are relative. Conditions and absolute yields for several typical reactions may be found in the Experimental Section. In all cases the amount of cis linear product (l or l') was <5%. [b] See Scheme I for drawings. [c] We found no *cis*-1-phenylpropene, phenylcyclopropane, or styrene. [d] We found no 1-methyl-2-phenylcyclopropane, *trans*-propenylbenzene, or styrene. [e] We found no 1,2-diphenylcyclopropane. [f] Similar yields were observed by using Ta(CHCMe$_3$)L$_2$Cl$_3$ (L = PPhMe$_2$, PPh$_2$Me), [Ta(CHCMe$_3$)(PMe$_3$)Cl$_3$]$_2$, Nb(CHCMe$_3$)(PMe$_3$)$_2$Cl$_3$, Nb(CHCMe$_3$)(PPhMe$_2$)$_2$Cl$_3$, and [Nb(CHCMe$_3$)(PMe$_3$)Cl$_3$]$_2$. [g] Similar yields were observed by using Ta(CHCMe$_3$)L$_2$Cl$_3$ and [Ta(CHCMe$_3$)LCl$_3$]$_2$ (L = PMe$_3$, PPhMe$_2$, PPh$_2$Me).

pentane complex.[5] Recently we have prepared other complexes which are suitable for studying this type of reaction, octahedral complexes of the type M(CHR)L$_2$X$_3$.[6] These species also react with terminal olefins to give "rearrangement" products. However, we now find they can be modified so that the rate of rearrangement of the intermediate tantallacyclobutane ring is slow relative to metathesis. This modification to give metathesis catalysts is the subject of this paper. Some of this work has appeared in preliminary form.[7]

Results

Reactions of Halo/Alkylidene Complexes with Ethylene, Propylene, or Styrene. Ta(CHR)L$_2$Cl$_3$ (R = CMe$_3$ or Ph, L = a tertiary phosphine) reacts within a few seconds with ethylene, propylene, or styrene to give *trans-mer*-Ta(olefin)L$_2$Cl$_3$ (see Experimental Section for details) and the four products of rearrangement of the two possible intermediate metallacyclobutane complexes (Scheme I; Table I). The product ratio is not affected significantly by the choice of phosphine, and niobium complexes or dimeric species of the type [M(CHCMe$_3$)LCl$_3$]$_2$ give similar organic products (Table I). We found that Ta(CHCMe$_3$)(PMe$_3$)$_2$Cl$_3$ reacted with ethylene in the presence of 1 equiv of 4,4-dimethyl-1-pentene to give a product mixture consisting of 1.1 equiv of 4,4-dimethyl-1-pentene and 0.9 equiv of *trans*-4,4-dimethyl-2-pentene; therefore once the olefin product dissociates from the metal, it is not isomerized. In no case do we observe any of the possible metathesis products. When Ta(CHPh)(PMe$_3$)$_2$Cl$_3$ was allowed to react with *p*-MeC$_6$H$_4$CH=CH$_2$ to ~50% completion, the remaining alkylidene complex was exclusively Ta(CHPh)(PMe$_3$)$_2$Cl$_3$ by ^{1}H NMR, as it should be if the rate of metathesis is slow relative to the rate of rearrangement of the intermediate metallacyclobutane complex. We also looked for cyclopropane products in several cases but found none. Since we do see all four possible rearrangement products, the initial postulate[5b] that the nucleophilic character of the alkylidene α-carbon atom determines what metallacycle forms and rearranges must be incorrect.

The reaction between Ta(CHCMe$_3$)(dmpe)Cl$_3$ and ethylene requires hours at 80–100 °C. Since phosphine ligands in Ta(CHCMe$_3$)(PR$_3$)$_2$Cl$_3$ are known to be labile,[6] we conclude that the olefin actually must coordinate to the metal before it can react with a neopentylidene or benzylidene ligand.

The organic products of the reaction between Ta(CHCMe$_3$)(THF)$_2$Cl$_3$ or Ta(CHCMe$_3$)(py)$_2$Cl$_3$ and ethylene are largely rearrangement products, but the mixture contains a reproducible amount of the metathesis product, 3,3-dimethyl-1-butene (6% and 15%, respectively). We were not able to observe the methylene complex which must form when the initial metallacycle loses 3,3-dimethyl-1-butene, nor could we determine its fate.

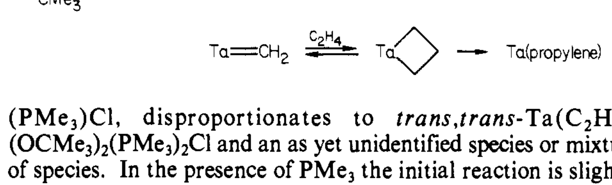
Preparation of Alkoxo Complexes and How They React with Ethylene. We turned to preparing and studying alkoxo complexes for two reasons. If metathesis by the THF or pyridine complexes can be attributed to the fact that THF and pyridine are "hard" donor ligands, then perhaps a "hard" covalently bonded ligand will promote metathesis even more effectively. Second, we noted that substituting a methoxide for a chloride made *tantallacyclopentane* complexes relatively stable toward rearrangement to an olefin by a β-hydride elimination process, one which proceeds via a *tantallacyclobutane* intermediate.[8]

M(CHCMe$_3$)(PMe$_3$)$_2$Cl$_3$ reacts with 2 equiv of LiOCMe$_3$ to give yellow M(CHCMe$_3$)(OCMe$_3$)$_2$(PMe$_3$)Cl in good yield (M = Nb or Ta). We suspect these molecules are trigonal bipyramids in which the neopentylidene ligand lies in the equatorial plane and the PMe$_3$ ligand is axial, on the basis of the structure of Ta(CHCMe$_3$)$_2$(mesityl)(PMe$_3$)$_2$.[9] However, we cannot choose between a molecule in which one of the inequivalent alkoxides is equatorial and one is axial and a molecule containing two equatorial alkoxides which are inequivalent by virtue of the fact that the neopentylidene ligand lies in the equatorial plane and does not rotate. We prefer the former proposal since there is one less 90° interaction between PMe$_3$ and the three *tert*-butyl-containing ligands. M(CHCMe$_3$)(OCMe$_3$)$_2$(PMe$_3$)Cl will coordinate a second PMe$_3$ ligand in the presence of a large excess of PMe$_3$ or at low temperatures in the presence of 1 equiv of PMe$_3$.

A mono-*tert*-butoxide complex can be prepared by reacting M(CH$_2$CMe$_3$)$_2$(OCMe$_3$)Cl$_2$ with PMe$_3$, a version of the reaction used to prepare M(CHCMe$_3$)(PMe$_3$)$_2$Cl$_3$.[6] The NMR data suggest that two isomers are formed and that the PMe$_3$ ligands are trans and equivalent in the major isomer.

Ta(CHCMe$_3$)(OCMe$_3$)$_3$ (cf. Ta(CHCMe$_3$)(CH$_2$CMe$_3$)$_3$[10]) can be prepared from Ta(CHCMe$_3$)(THF)$_2$Cl$_3$[6] and LiOCMe$_3$. It is a yellow-orange oil and therefore is not readily purified. Ta(CHCMe$_3$)(OCMe$_3$)$_3$ does not form a stable PMe$_3$ adduct at room temperature (by ^{31}P NMR).

Ta(CHCMe$_3$)(OCMe$_3$)$_2$(PMe$_3$)Cl reacts rapidly with ethylene (30 psi) to give 1 equiv of *tert*-butylethylene, 1 equiv of propylene, and 0.4 equiv of Ta(C$_2$H$_4$)(OCMe$_3$)$_2$(PMe$_3$)Cl. We see no products arising from rearrangement of the initial metallacyclobutane complex. We believe propylene is formed by rearrangement of the unsubstituted tantallacyclobutane complex which is formed from the intermediate methylene complex and ethylene (eq 1). Apparently, the initial complex, Ta(C$_2$H$_4$)(OCMe$_3$)$_2$(PMe$_3$)Cl, disproportionates to *trans,trans*-Ta(C$_2$H$_4$)(OCMe$_3$)$_2$(PMe$_3$)$_2$Cl and an as yet unidentified species or mixture of species. In the presence of PMe$_3$ the initial reaction is slightly slower and the yield of Ta(C$_2$H$_4$)(OCMe$_3$)$_2$(PMe$_3$)$_2$Cl is high.



(1)

Ta(CHCMe$_3$)(OCMe$_3$)(PMe$_3$)$_2$Cl$_2$ reacts with ethylene to give solely *rearrangement* products and an ethylene complex in high

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(5) (a) McLain, S. J.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 4558–4570. (b) *Ibid.* **1977**, *99*, 3519–3520.

(6) Rupprecht, G. A.; Messerle, L. W.; Fellmann, J. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 6236.

(7) Schrock, R.; Rocklage, S.; Wengrovius, J.; Rupprecht, G.; Fellmann, J. *J. Mol. Catal.* **1980**, *8*, 73–83.

(8) McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 5610–5618.

(9) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 1930–1935.

(10) Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359–3370.

Table II. Organic Products of the Reaction of $M(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ with Styrene, Propenylbenzene, and Stilbene[a]

	M[b]	olefin	time, h	*trans*-stilbene	*cis*-stilbene	*trans*-PhCH= CHCMe$_3$	*cis*-PhCH= CHCMe$_3$	Me$_3$-CCH= CH$_2$	*trans*-Me$_3$CCH= CHMe	% rxn[c]
1	Ta	PhCH=CH$_2$	2	2[d]	0[d]	6	0	69		75
2	Ta + L	PhCH=CH$_2$	7	0	0	0	0	80		80
3	Nb	PhCH=CH$_2$	2	0[e]	1[e]	3	0	69		72
4	Ta	*cis*-PhCH=CHMe	40	9	4	2	0		87[f]	>89
5	Nb	*cis*-PhCH=CHMe	40	24	2	8	0		86[f]	>94
6	Nb + L	*cis*-PhCH=CHMe	40	15	3	7	0		80[f]	>87
7	Nb	*cis*-PhCH=CHPh	2	27	21	91	8			99
8	Ta + L	*cis*-PhCH=CHPh	12	24	15	100	0			100
9	Ta + L	*trans*-PhCH=CHPh	16	82	2	24	1			25

[a] One equivalent of olefin at 25 °C in benzene. Yields of olefin products are in mol %. Usually the system was sampled six times over the course of the run. [b] L = PMe$_3$. [c] % rxn = the sum of all *tert*-butyl-containing metathesis products. [d] After 40 h *trans*-stilbene = 13%; *cis*-stilbene = 3%. [e] After 40 h *trans*-stilbene = 25%; *cis*-stilbene = 2%. [f] *cis*-Me$_3$CCH=CHMe is obscured in GLC traces.

yield (eq 2). The major isomer of the ethylene complex has trans, equivalent phosphine ligands.

$$\mathrm{Ta(CHCMe_3)(OCMe_3)(PMe_3)_2Cl_2 + C_2H_4 \xrightarrow{1\ h} Ta(C_2H_4)(OCMe_3)(PMe_3)_2Cl_2 +}$$
$$\mathrm{\mathit{t}\text{-}Me_3CCH{=}CHMe\ (24\%) + Me_3CCH_2CH{=}CH_2\ (65\%)} \tag{2}$$

$Ta(CHCMe_3)(OCMe_3)_3$ reacts only slowly with ethylene to give largely rearrangement products (eq 3). We could not isolate

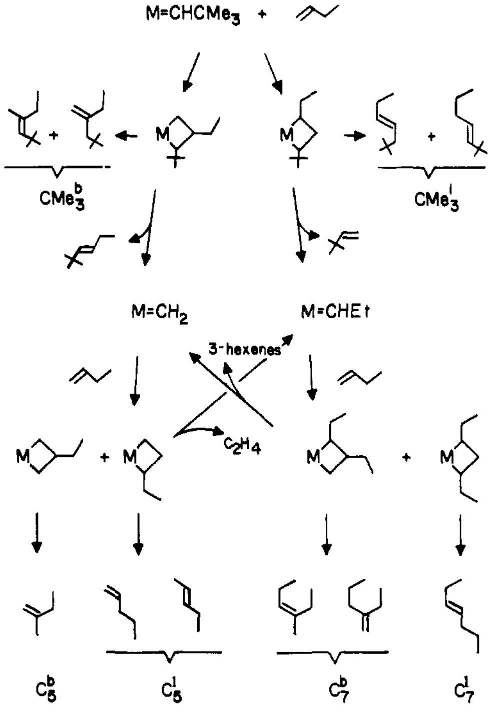
$$\mathrm{Ta(CHCMe_3)(OCMe_3)_3 + C_2H_4 \xrightarrow{8\ h}}$$
$$\mathrm{Me_3CCH_2CH{=}CH_2\ (57\%) + \mathit{t}\text{-}Me_3CCH{=}CHMe\ (29\%) + Me_3CCH{=}CH_2\ (4\%)} \tag{3}$$

or identify in situ any organometallic product. Adding PMe$_3$ to the system does not significantly change the results of the reaction with the neopentylidene ligand (13% metathesis, 66% rearrangement in 16 h), but now we also see 1-butene forming catalytically at a rate on the order of 0.5 equiv/h. We suspect that if forms via a tantallacyclopentane complex.[11]

Reactions of $M(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ with Styrene, Propenylbenzene, and Stilbene: Observation of the Transalkylidenation Reaction. We chose to look at the reaction of the di-*tert*-butoxy complexes with selected phenyl-substituted olefins since the product of the initial metathesis reaction could be an isolable benzylidene complex.

The organic products of several reactions are shown in Table II. The results can be summarized as follows. One equivalent of styrene reacts with $M(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ to give a good yield of the two possible initial metathesis products, most of which is 3,3-dimethyl-1-butene (Table II). *trans*- and *cis*-stilbenes form slowly in the absence of added PMe$_3$, probably primarily by intermolecular decomposition of the resultant benzylidene complex. The evidence consists of the fact that the amount of stilbenes continues to grow after the initial metathesis is complete and the fact that no stilbenes form in the presence of 1 equiv of PMe$_3$ (run 2). *cis*-Propenylbenzene reacts with $M(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ to give almost exclusively *trans*-4,4-dimethyl-2-pentene as the initial metathesis product. Stilbenes again form, more rapidly when M = Nb than when M = Ta and more slowly in the presence of PMe$_3$. *cis*-Stilbene reacts fairly quickly with both the Nb and Ta complexes to give the only possible initial metathesis product in good yield (runs 7 and 8). *trans*-Stilbene reacts much more slowly than *cis*-stilbene in the presence of PMe$_3$ (run 9 vs. run 8), as expected if the olefin must first compete with PMe$_3$ for a metal coordination site.

Scheme II. The Course of a Reaction between a Neopentylidene Complex and 1-Butene



In all of the above reactions we observe lime green $M(CHPh)(OCMe_3)_2(PMe_3)_2Cl$ as the major organometallic product. The yield in the presence of 1 equiv of PMe$_3$ when M = Ta is high, and it is easiest to isolate from the styrene reaction. It is six-coordinate, probably because the benzylidene ligand is not as sterically demanding as the neopentylidene ligand. However, the complex does lose one phosphine ligand readily in solution to give an orange complex which cannot be isolated free of stilbenes and organometallic decomposition products. By ^{13}C NMR we can show that this species is $[Ta(CHPh)(OCMe_3)_2(PMe_3)Cl]_x$. (We do not know if $x = 1$ or 2.) It decomposes readily to give stilbenes (eq 4). Mixtures of $Nb(CHPh)(OCMe_3)_2(PMe_3)_2Cl$ and $[Nb(CHPh)(OCMe_3)_2(PMe_3)Cl]_x$ can be observed in the reaction of $Nb(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ with styrene in the presence of PMe$_3$. The fact that we can prepare tantalum- and niobium-benzylidene complexes by a transalkylidenation reaction confirms that a new alkylidene complex forms whenever metathesis products are observed.

$$\mathrm{Ta(CHCMe_3)(OR)_2(PMe_3)Cl \xrightarrow[PMe_3]{PhCH{=}CH_2}}$$
$$\mathrm{Ta(CHPh)(OR)_2(PMe_3)_2Cl \xrightarrow{-PMe_3}}$$
$$\mathrm{{}^1/_{\mathit{x}}[Ta(CHPh)(OR)_2(PMe_3)Cl]_{\mathit{x}} \rightarrow stilbenes} \tag{4}$$
$$\mathrm{R = CMe_3}$$

Metathesis of 1-Butene: Why It Does Not Work. We developed a test for productive metathesis of a terminal olefin using 1-butene as the model since we could identify all metathesis or rearrangement products of initial or intermediate metallacyclobutane complexes. These products, and how they form, are shown in

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[11] This type of dimerization reaction was discovered first by using tantalum complexes of the type $Ta(\eta^5\text{-}C_5Me_5)(olefin)Cl_2$.[8] We will discuss these and similar results elsewhere since they are not of central interest to us here.

Table **III.** 1-Butene Test for Metathesis Activity[a]

		time, h	CMe$_3$^{b}	CMe$_3$^{1}	Me$_3$C-CH=CH$_2$	*trans*-Me$_3$C-CH=CHEt	% rxn	C$_5$^{b}	C$_5$^{1}	C$_7$^{b}	C$_7$^{1}	3-hexenes	decomp[b]	productive metathesis
1	Ta(CHCMe$_3$)(THF)$_2$Cl$_3$[c]	2		11	79		90			76		5	3	0
2	Nb(CHCMe$_3$)(THF)$_2$Cl$_3$	2		17	73		90			56		17	17	0
3	Ta(CHCMe$_3$)(py)$_2$Cl$_3$	2		38	51		89			20	27	0	4	0
4	Ta(CHCMe$_3$)(py)$_2$Cl$_3$ + py	48	22	53	17		92			5	7	0	5	0
5	Ta(CHCMe$_3$)(OCMe$_3$)·(PMe$_3$)$_2$Cl$_2$	1	7	50	32		89			15	20	<2	"−3"	0
6	Ta(CHCMe$_3$)(OCMe$_3$)$_2$·(PMe$_3$)Cl[d]	3			76	18	94	46				75	48	0
7	Nb(CHCMe$_3$)(OCMe$_3$)$_2$·(PMe$_3$)Cl	1/4			86	6	92					92	92	0
8	Nb(CHCMe$_3$)(OCMe$_3$)$_2$·(PMe$_3$)Cl + 2PMe$_3$[e]	1			97	1	98	55				202	43	104
9	Ta(CHCMe$_3$)OCMe$_3$[f]	6	7	73	17		97			9	6	<3	2	0

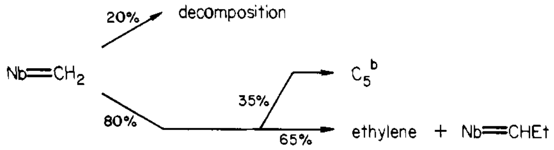
[a] The numbers are expressed as percent yield vs. the metal. Details can be found in the Experimental Section. [b] This number [Σ(initial metathesis products) − Σ(C$_5$^{b} + C$_5$^{1} + C$_7$^{b} + C$_7$^{1})] is accurate to only ca. ±5%. [c] Similar results were obtained with Ta(CHCMe$_3$)(DME)Cl$_3$ (DME = 1,2-dimethoxyethane). [d] 1-Butene dimers = 32%.[11] [e] The numbers did not change on varying the PMe$_3$ concentration from 1 to 10 equiv. Ethylene = 33%; theory = 125% − 104% by metathesis, 21% by decomposition of methylene complexes. [f] 1-Butene dimers = 40%.[11]

Scheme II, and the results for all complexes which yield at least some metathesis products are listed in Table III. Note that (i) metathesis of 1-butene is *productive* only if the amount of 3-hexenes exceeds the amount of 3,3-dimethyl-1-butene and (ii) the percent initial metathesis products less the sum of all products of rearrangement of intermediate metallacyclobutane complexes (C$_5$^{b}, C$_5$^{1}, C$_7$^{b}, C$_7$^{1}) equals the amount of chain termination by some other step which we call "decomposition".

THF- or pyridine-substituted neopentylidene complexes react with 1-butene to give more metathesis product than is formed when they react with ethylene, and it is all 3,3-dimethyl-1-butene. First, we note that when pyridine is added (reaction 4), the rate slows down, substantially less 3,3-dimethyl-1-butene is formed, and rearrangement of the α,β-disubstituted metallacycle (to give CMe$_3$^{b}) becomes important. Interestingly, metathesis of the initial α,β-disubstituted metallacycle does not compete with its rearrangement. Second, one or both of the two intermediate metallacycles which form from the intermediate propylidene complex and 1-butene mostly rearrange to C$_7$^{b} and C$_7$^{1}. When L = THF, metathesis of the α,β-diethylmetallacyclobutane complex competes with its rearrangement to give 5% (M = Ta) and 17% (M = Nb) 3-hexenes. Metathesis of the α,α'-diethylmetallacycle probably also competes with its rearrangement, but this process is degenerate. Third, the sum of C$_7$ rearrangement products and 3-hexenes approximately equals the amount of 3,3-dimethyl-1-butene, as it should if the metathesis chain never develops.

Ta(CHCMe$_3$)(OCMe$_3$)(PMe$_3$)Cl$_2$ reacts with 1-butene to yield some rearrangement and some metathesis products (run 5). The metathesis product is almost exclusively Me$_3$CCH=CH$_2$ and the new alkylidene therefore the propylidene complex. We have never been able to observe it by NMR since it apparently reacts too rapidly with more 1-butene to give the C$_7$ metallacycles which rearrange exclusively to the branched and linear C$_7$ olefins. These data suggest that the α-*tert*-butyl-α'-ethylmetallacyclobutane complex forms and metathesizes or rearranges more rapidly than the α-*tert*-butyl-β-ethylmetallacyclobutane complex. Note, however, that the rate of formation and rearrangement of the α,α'-diethylmetallacycle is about the same as that of the α,β-diethylmetallacycle.

The di-*tert*-butoxide complexes react with 1-butene to give only metathesis products (mostly Me$_3$CCH=CH$_2$; runs 6–8). First, note that intermediate C$_7$ metallacycles do *not* rearrange but *metathesize exclusively* to give 3-hexenes and an intermediate methylene complex. Second, one of the C$_5$ metallacycles which forms when the methylene complex reacts with 1-butene rearranges to a branched C$_5$ olefin, except in run 7 where decomposition of the Nb=CH$_2$ complex (we propose bimolecularly) is the fastest termination step. Third, by adding PMe$_3$ to the Nb catalyst, we can slow bimolecular decomposition so that some methylene complex survives to complete the catalytic metathesis cycle (run 8). If we say that 20% of the methylene complex decomposes each time and of the 80% that survives, 35% is converted into branched C$_5$ rearrangement products and 65% into ethylene and a propylidene complex by productive metathesis (eq 5), then after ten cycles all alkylidene complexes would be consumed. The yields of decomposition, rearrangement, and productive metathesis products would be 42%, 58%, and 108%, respectively. This is what we observe. We do observe some ethylene in solution, but no propylene, the likely product of rearrangement of a propylidene ligand. Apparently, this rearrangement is considerably slower than the other termination steps in this system (cf. metathesis of *cis*-2-pentene).



(5)

Ta(CHCMe$_3$)(OCMe$_3$)$_3$ reacts with 1-butene (run 9) to give mostly rearrangement products of the initial metallacycles and intermediate C$_7$ metallacycles.

Metathesis of *cis*-2-Pentene. Unlike the phosphine complexes, the THF and py complexes react (slowly) with *cis*-2-pentene. Ta(CHCMe$_3$)(THF)$_2$Cl$_3$ in the presence of THF yields one of the initial metathesis products, *trans*-2,2-dimethyl-3-hexene (30%). The other probably also forms but we cannot see it by GLC due to the presence of free THF in the mixture. 2-Butenes and 3-hexenes form catalytically but only about 6 equiv of each before the system deactivates (eq 6). We cannot be certain, on the basis

$$\mathrm{Ta(CHCMe_3)(THF)_2Cl_3} \xrightarrow[\text{2.5THF, ether, 4h}]{\textit{cis}\text{-2-pentene}} 0.30t\text{-}\mathrm{Me_3CCH{=}CHEt} + \sim 6 \text{ 3-hexenes} + \sim 6 \text{ 2-butenes} \quad (6)$$

of these data alone, that none of the initial metallacycle rearranges, but for us to see about 6 equiv of productive metathesis products, a significant percentage (>90%) of the initial and intermediate trisubstituted metallacyclobutane complexes must metathesize rapidly relative to the rate at which they rearrange.

The reaction between Ta(CHPh)(THF)$_2$Cl$_3$ (generated in 25% yield in situ from Ta(CH$_2$Ph)$_2$Cl$_3$ and THF in ether) and *cis*-2-pentene shows more clearly that the initial metallacycles metathesize in high yield and that 5–6 equivalents of 3-hexenes form (vs. Ta(CHPh)(THF)$_2$Cl$_3$ formed) before the reaction stops (eq 7). In this case, as well as the above, we do not know what the major chain-terminating reaction(s) is (are). However, we suspect that the intermediate propylidene and ethylidene complexes are

$$\mathrm{Ta(CH_2Ph)_2Cl_3} \xrightarrow[\text{4THF, ether}]{\textit{cis}\text{-2-pentene}} 0.25\text{toluene} + 0.21t\text{-PhCH=CHMe} + 0.05t\text{-PhCH=CHEt} + 1.4\ \text{3-hexenes} \quad (7)$$

prone to decompose bimolecularly since even $Ta(CHPh)(PMe_3)_2Cl_3$ decomposes fairly readily in this manner[6] and $Ta(CHPh)(THF)_2Cl_3$ has not yet been isolated.

cis-2-Pentene (100 equiv) reacts with $Nb(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ in the presence of PMe_3 to give the two initial metathesis products (90% combined yield) in 25 min (Figure 1). At the same time 2-butenes and 3-hexenes begin forming so that after 25 min 5–6 equiv of each are present (Figure 2). After 2 h about 15 equiv have formed and after 24 h about 34 equiv. *cis*-2-Pentene is rapidly isomerized during the metathesis reaction to *trans*-2-pentene (Figure 2). After 24 h the catalyst is no longer active; any added *cis*-2-pentene is neither metathesized nor isomerized.

An important finding is that propylene and ethylene appear early in the reaction along with the initial metathesis products (Figure 1). They must be formed by rearrangement of the intermediate propylidene and ethylidene complexes, respectively. Since at least 0.6 equiv form, bimolecular decomposition of intermediate alkylidene complexes and rearrangement of intermediate metallacycles both must be fairly slow; i.e., *rearrangement of intermediate alkylidene complexes must now be the major metathesis chain termination step.*

$Ta(CHCMe_3)(OCMe_3)_3$ reacts quickly with *cis*-2-pentene to give initial and productive metathesis products, but the system deactivates after about seven turnovers (Table IV). Adding monodentate tertiary phosphines increases the number of turnovers while adding a chelating phosphine (dmpe) appears to slow the formation of initial as well as productive metathesis products. We do *not* see any significant amount of ethylene or propylene nor any significant amount of metallacyclobutane rearrangement products. Therefore *if* there is no chain-terminating decomposition step we do not yet know about, bimolecular decomposition must be the primary chain termination step.

Discussion

The only olefin metathesis catalysts which contain niobium or tantalum are heterogeneous catalysts.[12] The scarcity of homogeneous catalysts might be ascribed to a failure to generate the initial alkylidene ligand by using techniques which are successful for preparing homogeneous group 6 metal catalysts. However, even if an alkylidene complex were generated, it now seems likely that the metathesis chain, as we have found here, would be terminated by bimolecular decomposition of alkylidene complexes (especially of methylene complexes), rearrangement of metallacyclobutane rings to olefins, and rearrangement of alkylidene ligands to olefins. While we cannot be certain that similar steps terminate the metathesis chain in classical metathesis systems, all have been mentioned as possible termination steps[2] and the probability that at least one of them is an important chain termination step seems high. The fact that we never see cyclopropanes, however, augurs poorly for them as chain termination products in the classical systems.

There are two conclusions concerning the formation and metathesis of metallacyclobutane complexes we feel are justified. The first is that α,α'-disubstituted metallacycles form and metathesize faster than α,β-disubstituted metallacycles. This is one of the two possible ways methylene groups in terminal olefins can scramble rapidly relative to productive metathesis, a phenomenon which has been known for several years in classical metathesis systems.[2] Unfortunately, this result does not help settle the debate as to whether formation and metathesis of α,α'-disubstituted metallacycles or β-monosubstituted metallacycles is the faster means of scrambling methylene groups. The second conclusion is that α,β,α'-trisubstituted metallacycles rearrange much more slowly *relative to* the rate they metathesize than di- or monosubstituted metallacycles.

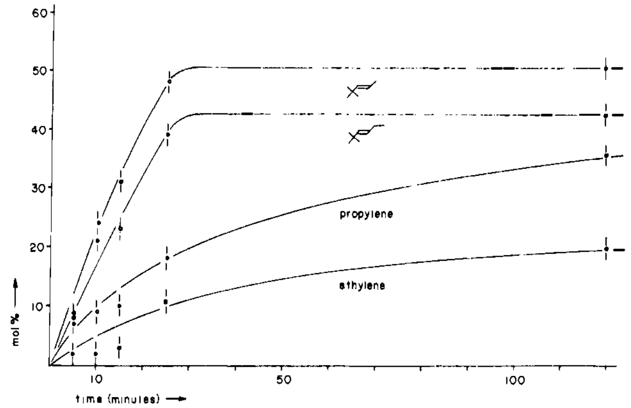


Figure 1. Cleavage and alkylidene rearrangement products in the metathesis of *cis*-2-pentene with $Nb(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ in the presence of PMe_3 in mesitylene at 25 °C. (The mole percents of ethylene and propylene are inaccurate and low, especially initially, due to loss of these products in the gas phase.)

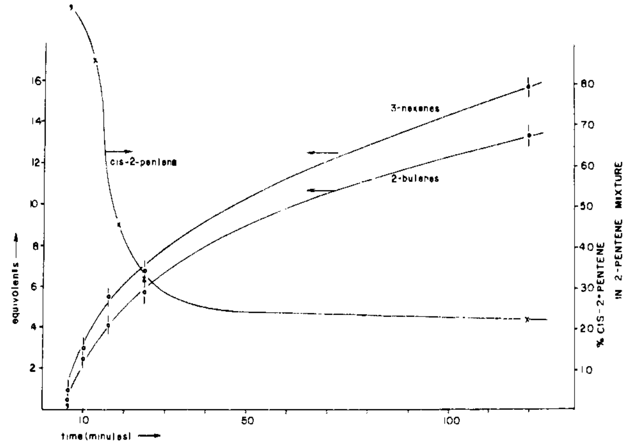


Figure 2. Metathesis of *cis*-2-pentene by $Nb(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ in the presence of PMe_3 in mesitylene at 25 °C. (Equivalents of butene are low due to experimental difficulties. After 24 h, 34 equiv of 3-hexenes and 29 equiv of 2-butenes had formed.)

Table IV. Metathesis of *cis*-2-Pentene by $Ta(CHCMe_3)(OCMe_3)_3$[a]

added ligands[b]	time	initial products,[c] %	3-hexenes, %
none	15 min	79	700[d]
$PPhMe_2$	30 min	91	1060[d]
PEt_3	30 min	97	860[d]
PMe_3	2 h	73	1200
	16 h	78	1600
dmpe[h]	30 min[e]		270
	1 h		370
	2 h[f]	28	550
	10 h[g]	32	810

[a] 50 mg of complex in toluene at ca. 25 °C plus ca. 50 equiv of *cis*-2-pentene. 2-Butenes were not measured unless otherwise noted. [b] Ca. 50 mg. [c] Roughly equal amounts of *trans*-4,4-dimethyl-2-pentene and *trans*-2,2-dimethyl-3-hexene. [d] No substantial further activity. [e] *cis*-2-Butene = 250%; *trans*-2-butene = 45%. [f] *cis*-2-Butene = 410%; *trans*-2-butene = 130%. [g] *cis*-2-butene = 415%; *trans*-2-butene = 335%. [h] dmpe = $Me_2PCH_2CH_2PMe_2$.

One of the most important of our results is that replacing chloride ligands with alkoxide ligands tends to slow down the rate of rearrangement of a metallacyclobutane ring relative to metathesis. We stress that this is only a trend. Obviously, other factors such as coordination number, types of donor ligands, and structures of metallacycles will also be important. (Almost certainly, this is why the behavior of $Ta(CHCMe_3)(OCMe_3)_3$ is somewhat inconsistent compared to that of $Ta(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ and $Ta(CHCMe_3)(OCMe_3)(PMe_3)_2Cl_2$.)

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(12) Bailey, G. C. *Catal. Rev.* **1969**, *3*, 37.

The important question is whether the rate of rearrangement of a metallacyclobutane ring slows down absolutely. We believe it does on the basis of the fact that the rate of rearrangement of a *tantallacyclopentane* ring to an olefin (a β-hydride elimination process which leads to a *tantallacyclobutane* ring which subsequently rearranges[8]) slows by a factor of $\sim 2 \times 10^{-2}$ on replacing one chloride ligand in the olefin dimerization catalyst by a methoxide ligand. Since rearrangement of metallacycles to olefins involves formally a reduction of the metal, it is reasonable that an alkoxide, which is compatible with a d^0 metal, should "stabilize" a d^0 metallacycle toward rearrangement to a d^2 olefin complex. Although there are few data concerning how general a phenomenon in early transition-metal organometallic chemistry this "alkoxide effect" might be, it is worth noting that some of the earliest stable d^0 metal alkyls (e.g., $Ti(O$-*i*-$Pr)_3Ph$, 1952[13]) contain alkoxide ligands.[14]

Our results encouraged us to attempt to make isoelectronic group 6 alkylidene complexes containing ligands which stabilize high oxidation states. These experiments led to the discovery of oxoalkylidene[7,15] and imidoalkylidene[16] complexes, which, we were pleased to find, also metathesize olefins.[15] Therefore we believe that many, if not most, metathesis catalysts are d^0 complexes (counting the alkylidene ligand as a dianion) in which there are enough "hard" π-electron donor ligands to sustain the d^0 oxidation state. Other recent results by Osborn[17] and Goddard,[18] as well as earlier work by Bassett[19] and Muetterties,[20] are consistent with this proposal.

Experimental Section

All preparative work was done in a nitrogen-filled drybox. General techniques of solvent purification etc. can be found elsewhere.[4,5] Octahedral neopentylidene and benzylidene complexes were prepared by published methods.[6] GLC yields were determined by the internal standard method. Organic products were identified by GLC and ^1H or ^{13}C NMR comparison with authentic samples. All NMR data are given in parts per million from Me_4Si (^1H and ^{13}C) or H_3PO_4 (^{31}P). The sample temperature was ca. 30 °C unless otherwise noted. ^{13}C NMR spectra were run both in the proton-decoupled mode and the gated decoupled mode (unless otherwise noted) to obtain all coupling constants accurately. NMR frequencies are 90 MHz (^1H), 15 or 22.63 MHz (^{13}C), and 36 MHz (^{31}P) unless otherwise noted.

Reactions of Alkylidene Complexes with Olefins. A minimum of ca. 0.5 mmol of complex was dissolved in 5–10 mL of ether or benzene containing an internal GLC standard (e.g., heptane or octane) and treated with ethylene or propylene in a pressure bottle or with excess styrene in a capped vial in the drybox. The slower reactions (e.g., $Ta(CHPh)(PMe_3)_2Cl_3$ with olefins; see below) were heated to ca. 45 °C. Samples were withdrawn and air oxidized before being analyzed by GLC. Samples from reactions involving *tert*-butoxide complexes were passed down a short alumina column (followed by solvent rinses) to free them of *tert*-butyl alcohol since it interfered with the GLC analysis for 3,3-dimethyl-1-butene. Absolute yields of rearrangement of initial metathesis products were >90% unless less than ca. 0.25 mmol of complex was used; we believe trace amounts of oxygen and water often react with the starting alkylidene complex in such cases.

Metathesis reactions in which ethylene or 2-butenes were produced were sampled with a cold syringe. Most reactions were run in serum-capped vials.

We report only a few reactions in detail here. Yields of organic products are summarized in the text.

Reactions of $Ta(CHCMe_3)(PMe_3)_2Cl_3$ with Olefins. (a) Ethylene. A solution of $Ta(CHCMe_3)(PMe_3)_2Cl_3$ (2.04 g, 4.00 mmol) in 10 mL of ether containing heptane (1.00 mmol of internal standard) was placed in a pressure bottle and stirred at 22 °C for 3 h under 50 psi of ethylene. The purple solution quickly turned blue. The volatiles were collected by trap-to-trap distillation under vacuum. They contained 0.06 equiv of 4,4-dimethyl-1-pentene and 0.92 equiv of *trans*-4,4-dimethyl-2-pentene. Blue $Ta(C_2H_4)(PMe_3)_2Cl_3$ was recrystallized from ether/pentane at −30 °C to give royal blue needles: yield 1.8 g (quantitative); ^1H NMR (C_6D_6) δ 2.88 (t, 4, $^3J_{HP} = 2.4$ Hz, C_2H_4), 1.47 (t, 18, $^2J_{HP} = 4.3$ Hz, PMe_3); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 59.0 (t, $^2J_{CP} = 3$ Hz, C_2H_4), 14.4 (t, $J_{CP} = 13$ Hz, PMe_3); $^{31}P\{^1H\}$ NMR (toluene, −30 °C) δ −4.1 (s). UV–vis (pentane) 243 (ϵ 2400), 317 (3400), 605 (53) nm.

Anal. Calcd for $TaC_8H_{22}Cl_3P_2$: C, 20.56; H, 4.74; P, 13.24. Found: C, 20.64; H, 4.08; P, 13.44.

(b) Propylene. A procedure similar to that in a gave 1.36 g of blue-black $Ta(propylene)(PMe_3)_2Cl_3$ from 1.53 g of $Ta(CHCMe_3)(PMe_3)_2Cl_3$. The volatiles contained 0.08 equiv of 2,4,4-trimethyl-1-pentene, 0.42 equiv of *trans*-5,5-dimethyl-3-hexene, 0.07 equiv of *trans*-5,5-dimethyl-2-hexene, and 0.41 equiv of 2,4,4-trimethyl-2-pentene. ^1H NMR (C_6D_6): δ 3.59 (m, 1, $CH_2{=}CHMe$), 3.28 (m, 2, $CH_2{=}CHMe$), 1.55 (m, 9, PMe_3), 1.46 (m, 9, PMe_3'), 1.12 (m, 3, $CH_2{=}CHMe$).

(c) Styrene. A procedure similar to that in a employing 1.53 g (3.00 mmol) of $Ta(CHCMe_3)(PMe_3)_2Cl_3$ and 1.25 g of styrene produced a blue solution after 8 h at 25 °C. The volatiles contained 0.35 equiv of (*Z*)-2-phenyl-4,4-dimethyl-2-pentene, 0.29 equiv of *trans*-1-phenyl-4,4-dimethyl-2-pentene, 0.30 equiv of *trans*-1-phenyl-4,4-dimethyl-1-pentene, and 0.06 equiv of 2-phenyl-4,4-dimethyl-1-pentene. The crude product was recrystallized from toluene/pentane at −30 °C to give blue-green crystals from a blue solution: yield 1.52 g (93%); ^1H NMR (C_6D_6, 270 MHz) δ 6.62–7.31 (m, 5, Ph), 4.49 (m, 1, $CH_2{=}CHPh$), 3.84 (m, 1, $CH_2{=}CHPh$), 2.81 (m, 1, $CH_2{=}CHPh$), 1.46 (dd, 9, $J_{HP} = 7.5$ Hz, $J_{HP'} = 1.2$ Hz, PMe_3), 1.33 (dd, 9, $J_{HP} = 7.5$ Hz, $J_{HP'} = 1.1$ Hz, PMe_3'). At 90 MHz and 132 °C the two PMe_3 peaks just coalesce. In the presence of free PMe_3 these peaks average with that for free PMe_3 at this temperature.

Reaction of $Ta(CHPh)(PMe_3)_2Cl_3$ with Olefins. (a) Ethylene. A benzene solution (10 mL) containing 0.54 g of $Ta(CHPh)(PMe_3)_2Cl_3$ (1.0 mmol) was stirred under 50 psi of ethylene at 45 °C for 4 h. GLC analysis of an air-oxidized sample showed 3-phenyl-1-propene (0.68 mmol) and *trans*-1-phenylpropene (0.25 mmol). Sublimation of the royal blue inorganics from a 1.89 mmol reaction gave 0.60 g (68% yield) of $Ta(C_2H_4)(PMe_3)_2Cl_3$.

(b) Propylene. The procedure is the same as that in a but is for 2 h at 50 °C. GLC analysis showed 3-phenyl-2-methylpropene (0.331 mmol, 33%), 4-phenyl-2-butene (0.033 mmol, 3%), 1-phenyl-2-methylpropene (0.141 mmol, 14%), and *trans*-1-phenylbutene (0.179 mmol, 18%), and no 1-methyl-2-phenylcyclopropane.

(c) Styrene. The procedure is the same as that in a but uses 0.31 g (3 mmol) of styrene for 2 h at 50 °C. GLC analysis showed *cis*-methylstilbene (0.34 mmol, 34%), two minor peaks (ca. 0.04 mmol total, 4%) assigned to 2,3-diphenylpropene and *cis*-1,3-diphenylpropene, *trans*-methylstilbene (0.069 mmol, 7%), and *trans*-1,3-diphenylpropene (0.32 mmol, 32%). Coinjection with an authentic sample ruled out the presence of 1,2-diphenylpropene. ^1H NMR showed that the major products were the methylstilbenes and *trans*-1,3-diphenylpropene by comparison to spectra of authentic samples.

(d) *p*-Methylstyrene. A mixture of $Ta(CHPh)(PMe_3)_2Cl_3$ (1.06 g, 2.00 mmol) and 4-methylstyrene (0.47 g, 4.0 mmol) after several days was air oxidized and then passed through activated alumina (followed by an ether rinse). The products giving rise to the last two partially merged peaks in the GLC trace were collected by preparative GLC. The ^{13}C NMR spectrum of this fraction at 67.89 MHz was identical with that of the GLC purified mixture made by condensing phenylacetaldehyde with *p*-tolylacetaldehyde. The ^{13}C NMR spectrum of authentic *trans*-1-*p*-tolyl-3-phenylpropene was identical with that of one of the components of the tantalum mixture; the sample was made by Wittig reaction, was purified by preparative GLC, and was shown to be the trans isomer by IR.

Reaction of $Nb(CHCMe_3)(PMe_3)_2Cl_3$ with Ethylene. A solution of $Nb(CHCMe_3)(PMe_3)_2Cl_3$ (0.15 g, 0.36 mmol) in 5 mL of ether was placed in a pressure bottle and exposed to 50 psi of ethylene without stirring at room temperature for 8 h. (If the reaction is stirred, the product comes out of solution in a very finely divided microcrystalline form.) The purple solution became nearly colorless as violet crystals formed. The product was collected by filtration, rinsed with ether, and dried in vacuo. A GLC sample of the reaction solution contained 0.03 equiv of 4,4-dimethyl-1-pentene and 0.90 equiv of *trans*-4,4-dimethyl-2-pentene.

An identical complex could be obtained as follows. A toluene solution (20 mL) of $NbCl_5$ (1.35 g, 5.0 mmol) was cooled to −30 °C. PMe_3 (1.52 g, 20 mmol) was added to give a precipitate of the orange PMe_3 adduct.

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(13) Herman, D. F.; Nelson, W. K. *J. Am. Chem. Soc.* **1952**, *74*, 2693; **1953**, *75*, 3882, 3877.

(14) Schrock, R. R.; Parshall, G. W. *Chem. Rev.* **1976**, *76*, 243–268.

(15) Wengrovius, J. H.; Schrock, R. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 4515–4516.

(16) S. Pedersen, unpublished results.

(17) Kress, J. R. M.; Russell, M. J. M.; Wesolek, M. G.; Osborn, J. A. *J. Chem. Soc. Chem. Commun.* **1980**, 431–432.

(18) Rappe, A. K.; Goddard, W. A. *J. Am. Chem. Soc.* **1980**, *102*, 5115–5117.

(19) Bassett, J. M.; Coudurier, G.; Muten, R.; Praliand, H. *J. Catal.* **1974**, *34*, 152.

(20) Mocella, M. T.; Rovner, R.; Muetterties, E. L. *J. Am. Chem. Soc.* **1976**, *98*, 4689–4690.

Sodium amalgam (0.83%, 27.7 g, 10 mmol) was added, and the reaction mixture was warmed to 25 °C and vigorously stirred for 1.5 h. The red solution was filtered through Celite, and the volume was reduced (in vacuo) to ~10 mL. Trituration with pentane (5 mL) gave 1.0 g of purple crystals. An analytically pure sample was obtained by multiple recrystallizations from concentrated dichloromethane solutions at −30 °C. It was shown to be $[Nb(PMe_3)_2Cl_3]_x$, an analogue of which has been prepared by Riess.[21] ^{1}H NMR (CH_2Cl_2): δ 1.67 (br m, PMe_3), 1.22 (br s, PMe_3).

Anal. Calcd for $NbC_6H_{18}Cl_3P_2$: C, 20.50; H, 5.16. Found: C, 20.48; H, 5.19.

Reaction of $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$ with Ethylene. A toluene solution (100 mL) of $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$ (2.17 g, 2.51 mmol) was placed under 50 psi of ethylene without stirring for 1 day. Dark blue crystals formed slowly in the blue solution (40 mg after 1 day). (A GLC sample of the reaction solution showed it to contain 0.05 equiv of 4,4-dimethyl-1-pentene and 0.93 equiv of *trans*-4,4-dimethyl-2-pentene.) The volume of the filtrate was reduced to 40 mL, and pentane was added to precipitate a violet powder (1.16 g): total yield 1.20 g (59%) of $[Ta(C_2H_4)(PMe_3)Cl_3]_x$; ^{1}H NMR (toluene-$d_8$) δ 3.04 (m, olefinic H), 1.35 (d, $^2J_{HP}$ = 9.0 Hz, PMe_3).

$[Ta(C_2H_4)(PMe_3)Cl_3]_x$ (1.56 g, 2 mmol) was suspended in 10 mL of benzene, and PMe_3 (0.16 g, 2.1 mmol, 5% excess) was added. The solvent and excess PMe_3 were removed in vacuo to give blue needles of $Ta(C_2H_4)(PMe_3)_2Cl_3$.

Proof of Structures of Olefin Complexes. Addition of 1 equiv of PMe_2Ph to $[Ta(C_2H_4)(PMe_3)Cl_3]_x$ yields a mixture of $Ta(C_2H_4)(PMe_3)_2Cl_3$ (~1 part), $Ta(C_2H_4)(PMe_3)(PMe_2Ph)Cl_3$ (~3 parts), and $Ta(C_2H_4)(PMe_2Ph)_2Cl_3$ (2 parts). The ^{31}P NMR spectrum of this mixture shows that $J_{PP'}$ = 150 Hz in $Ta(C_2H_4)(PMe_3)(PMe_2Ph)Cl_3$, consistent with the trans formulation. In the ^{13}C NMR spectrum the olefinic carbon atoms are inequivalent and do not begin to equilibrate rapidly on the NMR time scale until high temperatures, where we know coordinated phosphine exchanges rapidly with free phosphine. Therefore the metal–ethylene plane must contain the P–Ta–P′ axis, and ethylene must *not* rotate readily about the ethylene–metal bond axis ($\Delta G^{\ddagger} \geq$ ca. 20–25 kcal mol^{-1}).

Preparation of $Ta(CH_2CMe_3)_2(OCMe_3)Cl_2$. $Ta(CH_2CMe_3)_2Cl_3$ (2.15 g, 5.00 mmol) in 50 mL of ether reacts slowly with $Mg(OCMe_3)Cl$ (0.68 g, 5.13 mmol; prepared from BuMgCl and *tert*-butyl alcohol in ether) to give a yellow solution containing gelatinous $MgCl_2$. After 12 h the reaction mixture was filtered, and the solvent was removed in vacuo, leaving an oily residue. The residue was extracted with hexane (30 mL), and the extract was filtered. The solvent was removed again in vacuo to give yellow crystals which were recrystallized from a concentrated pentane solution at −30 °C (24 h): yield 1.85 g (79%); ^{1}H NMR (C_6D_6, 270 MHz) δ 2.294 (d, 2, $^2J_{H_AH_B}$ = 10.76 Hz, C*H*$_A$H$_B$CMe$_3$), 1.801 (d, 2, $^2J_{H_BH_A}$ = 10.75 Hz, CH$_A$*H*$_B$CMe$_3$), 1.308 (s, 9, OCMe$_3$), 1.150 (s, 18, CH$_2$C*Me*$_3$); ^{13}C NMR (C_6D_6) δ 104.6 (t, $^1J_{CH}$ = 118 Hz, *C*H$_2$CMe$_3$), 36.3 (s, CH$_2$*C*Me$_3$), 35.3 (q, $^1J_{CH}$ = 125 Hz, CH$_2$C*Me*$_3$), 30.1 (q, $^1J_{CH}$ = 127 Hz, OC*Me*$_3$). C_β of the OCMe$_3$ group was not located.

Preparation of $Ta(CHCMe_3)(OCMe_3)(PMe_3)_2Cl_2$. $Ta(CH_2CMe_3)_2(OCMe_3)Cl_2$ (0.47 g, 1.0 mmol) reacts with PMe_3 (0.2 mL, excess) in CH_2Cl_2 (~10 mL) in 12 h to give an orange solution. The solvent was removed in vacuo, and the orange residue was extracted with hexane (~20 mL) and filtered. The solvent volume was reduced in vacuo until crystals appeared. Cooling to −30 °C for 2 h gave 0.44 g of product: yield (80%); ^{1}H NMR (toluene-d_8, 270 MHz, −50 °C) [major isomer] δ 9.19 (t, 1, $^2J_{HP}$ = 3.3 Hz, C*H*CMe$_3$), 1.33 (t, 18, $^2J_{HP}$ = 4.0 Hz, PMe$_3$), 1.30 (s, 9, OCMe$_3$), 1.14 (s, 9, CHC*Me*$_3$), [minor isomer] δ 8.11 (t, 1, $^2J_{HP} \approx$ 2.4 Hz, C*H*CMe$_3$), 1.19 (s, 9, CHC*Me*$_3$) (the major/minor isomer ratio was 13:1); ^{13}C NMR (toluene-d_8, 67.89 MHz, −50 °C) [major isomer] δ 281.7 (dt, $^2J_{CP}$ = 8.4 Hz, $^1J_{CH}$ = 110 Hz, *C*HCMe$_3$), 85.6 (s, O*C*Me$_3$), 42.9 (s, CH*C*Me$_3$), 36.3 (q, $^1J_{CH}$ = 125 Hz, CHC*Me*$_3$), 32.0 (q, $^1J_{CH}$ = 128 Hz, OC*Me*$_3$), 15.9 (qt, $^1J_{CP}$ = 12.3 Hz, $^1J_{CH}$ = 131 Hz, PMe$_3$), [minor isomer] 82.9 (s, O*C*Me$_3$), 44.0 (s, CH*C*Me$_3$), 30.4 (q, $^1J_{CH}$ = 128 Hz, OC*Me*$_3$), 15.9 (t, $^2J_{CP} \approx$ 14 Hz, PMe$_3$); ^{31}P{^{1}H} NMR (toluene-d_8, 109 MHz, −50 and 30 °C) [major isomer] δ −5.7 (s), [minor isomer] δ −10.1 (s).

Preparation of $Ta(C_2H_4)(OCMe_3)(PMe_3)_2Cl_2$. $Ta(CHCMe_3)(OCMe_3)(PMe_3)_2Cl_2$ (2.66 g, 4.86 mmol) was dissolved in ether (25 mL), and the solution was pressurized with ethylene (30 psi). The reaction mixture was heated at 50 °C for 1 h. Ether (~50 mL) was added to the cooled reaction mixture, and the solution was filtered. The solvent was removed in vacuo, and the residue was dissolved in a minimal amount of ether which contained 10% hexane. Standing the solution at −30 °C for 12 h gave 1.55 g of orange crystals (59% yield): ^{1}H NMR (C_6D_6, 270 MHz) [major isomer] δ 2.175 (m, 2, olefinic H), 1.591 (m, 2, olefinic H), 1.397 (t, 18, $^2J_{HP}$ = 3.9 Hz, PMe$_3$), 0.724 (s, 9, OCMe$_3$), [minor isomer] δ 0.738 (s, OC*Me*$_3$); ^{13}C NMR (C_6D_6) δ 83.3 (s, O*C*Me$_3$), 44.7 (tt, $^2J_{CP}$ = 3.7 Hz, $^1J_{CH}$ = 152 Hz, C$_2$H$_4$), 30.4 (q, $^1J_{CH}$ = 126 Hz, OC*Me*$_3$), 14.3 (qt, $^1J_{CP}$ = 11.7 Hz, $^1J_{CH}$ = 123 Hz, PMe$_3$).

Anal. Calcd for $TaC_{12}H_{31}Cl_2P_2O$: C, 28.53; H, 6.19. Found: C, 28.71; H, 6.23.

Preparation of $Ta(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$. $LiOCMe_3$ (0.80 g, 10 mmol) in 10 mL of ether was added dropwise to a stirred solution of $Ta(CHCMe_3)(PMe_3)_2Cl_3$ (2.55 g, 5 mmol) in 20 mL of ether at −30 °C. As the purple reaction mixture was allowed to warm to 25 °C, LiCl precipitated and the solution became yellow. After 2 h at 25 °C the mixture was filtered and the ether was removed from the filtrate in vacuo to give a yellow solid (2.4 g). The solid was dissolved in pentane, and the solution was treated with activated charcoal and filtered. Concentrating and cooling the pentane solution to −30 °C gave light yellow crystals of $Ta(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ (1.65 g, 65%). Samples sometimes contain $Ta(CHCMe_3)(OCMe_3)_2(PMe_3)_2Cl$ which can be converted to $Ta(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ by exhaustively removing excess PMe_3 in vacuo from a toluene solution before recrystallizing from pentane: ^{1}H NMR (toluene-d_8, 270 MHz, −60 °C) δ 9.392 (d, 1, $^3J_{HP}$ = 3.3 Hz, C*H*CMe$_3$), 1.405 (s, 9, OCMe$_3$), 1.375 (s, 9, OCMe$_3$′), 1.253 (s, 9, CHC*Me*$_3$), 1.082 (d, 9, $^2J_{HP}$ = 7.3 Hz, PMe$_3$); ^{13}C NMR (toluene-d_8, 67.89 MHz) δ 273.2 (dd, $^2J_{CP}$ = 2.9 Hz, $^1J_{CH}$ = 114 Hz, *C*HCMe$_3$), 80.7 (s, O*C*Me$_3$), 79.8 (s, O*C*Me$_3$′), 41.6 (s, CH*C*Me$_3$), 35.2 (q, $^1J_{CH}$ = 129 Hz, CHC*Me*$_3$), 32.5 (q, $^1J_{CH}$ = 125 Hz, OC*Me*$_3$), 32.3 (q, $^1J_{CH}$ = 125 Hz, OC*Me*$_3$′) 16.4 (qd, $^1J_{CP}$ = 21.1 Hz, $^1J_{CH}$ = 130 Hz, PMe$_3$); ^{31}P{^{1}H} NMR (toluene-d_8) δ 1.0 (s); IR (Nujol, NaCl) 2720 (vw, ν_{CH_α})cm^{-1}; M_r (cyclohexane, cryoscopically) Calcd 509, found 493.

Anal. Calcd for $TaC_{16}H_{37}O_2ClP$: C, 37.77; H, 7.33. Found: C, 37.84; H, 7.45.

$Ta(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ (0.25 mmol) reacted immediately with a twofold excess of sieve-dried reagent acetone to give 0.8 equiv of 2,4,4-trimethyl-2-pentene.

Preparation of $Nb(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$. Bright yellow $Nb(CHCMe_3)(OCMe_3)_2Cl(PMe_3)$ can be prepared by a procedure analogous to that used to prepare $Ta(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$: ^{1}H NMR (toluene-$d_8$, 270 MHz, −60 °C) δ 11.644 (d, $^3J_{HP} \approx$ 3 Hz, C*H*CMe$_3$), 1.411 (s, 9, OCMe$_3$), 1.354 (s, 9, OCMe$_3$′), 1.191 (s, 9, CHC*Me*$_3$), 1.012 (d, 9, $^2J_{HP}$ = 6.8 Hz, PMe$_3$); ^{13}C{^{1}H} NMR (toluene-d_8, 67.89 MHz, −25 °C) δ ~293 (b, *C*HCMe$_3$), 81 (s, O*C*Me$_3$), 80.2 (s, O*C*Me$_3$′), 43.1 (s, CH*C*Me$_3$), 33.5 (s, CHC*Me*$_3$), 32.6 (s, OC*Me*$_3$), 32.0 (s, OC*Me*$_3$′), 15.6 (d, $^1J_{CP}$ = 18.3 Hz, PMe$_3$); ^{31}P{^{1}H} NMR (toluene-d_8, −80 °C) δ −10 (br s).

Observation of $Ta(CHCMe_3)(OCMe_3)_2(PMe_3)_2Cl$. Addition of excess PMe_3 to a sample to $Ta(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ yielded $Ta(CHCMe_3)(OCMe_3)_2(PMe_3)_2Cl$ in situ at low temperatures. At room temperature the ratio of $Ta(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ to $Ta(CHCMe_3)(OCMe_3)_2(PMe_3)_2Cl$ depended upon the amount of excess PMe_3, sample concentration, etc.: ^{1}H NMR (toluene-d_8, 270 MHz, −45 °C) δ 9.149 (t, 1, $^3J_{HP}$ = 3.37 Hz, C*H*CMe$_3$), 1.476 (s, 9, OC*Me*$_3$), 1.450 (s, 9, OC*Me*$_3$′), 1.269 (t, 18, $^2J_{HP}$ = 3.0 Hz, PMe$_3$), 1.208 (s, 9, CHC*Me*$_3$); ^{13}C NMR (toluene-d_8, 67.89 MHz, −45 °C) δ 275.1 (dt, $^2J_{CP} \approx$ 8 Hz, $^1J_{CH} \approx$ 123 Hz, *C*HCMe$_3$), 79.8 (s, O*C*Me$_3$), 78.8 (s, O*C*Me$_3$′), 43.1 (s, CH*C*Me$_3$), 36.0 (q, $^1J_{CH}$ = 130 Hz, CHC*Me*$_3$), 32.9 (q, $^1J_{CH}$ = 123 Hz, OC*Me*$_3$), 32.3 (q, $^1J_{CH}$ = 123 Hz, OC*Me*$_3$′), 16.3 (qt, $^1J_{CP}$ = 11.5 Hz, $^1J_{CH}$ = 133 Hz, PMe$_3$); ^{31}P NMR (toluene-d_8, −60 °C) δ −14 (s).

At 25 °C PMe_3 is not exchanging rapidly with coordinated PMe_3 in either $Ta(CHCMe_3)(OCMe_3)_2(PMe_3)_2Cl$ or $Ta(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ by ^{31}P NMR, but only a trace of $Ta(CHCMe_3)(OCMe_3)_2(PMe_3)_2Cl$ is present. At 0 °C significantly more $Ta(CHCMe_3)(OCMe_3)_2(PMe_3)_2Cl$ is present, and at −60 °C $Ta(CHCMe_3)(OCMe_3)_2(PMe_3)_2Cl$ is by far the major component; it is the only one if several equivalents of PMe_3 have been added. This property causes some problems if $Ta(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ is crystallized at low temperatures in the presence of PMe_3. Only by slowly removing all volatiles at room temperature can one obtain a pure sample of $Ta(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ consistently.

Observation of $Nb(CHCMe_3)(OCMe_3)_2(PMe_3)_2Cl$. The sample behavior is the same as that noted for Ta above: ^{1}H NMR (toluene-d_8, 270 MHz, −45 °C) δ 11.547 (t, 1, $^3J_{HP}$ = 4.2 Hz, C*H*CMe$_3$), 1.478 (s, 18, OCMe$_3$), 1.209 (t, 18, $^2J_{HP}$ = 2.7 Hz, PMe$_3$), 1.144 (s, 9, CHC*Me*$_3$); ^{13}C{^{1}H} NMR (toluene-d_8, 67.89 MHz, −25 °C) δ ~293 (br, *C*HCMe$_3$), 80.4 (s, O*C*Me$_3$), 79.4 (s, O*C*Me$_3$′), 44.4 (s, CH*C*Me$_3$), 33.5 (s, CHC*Me*$_3$), 32.7 (s, OC*Me*$_3$), 32.2 (s, OC*Me*$_3$′), 16.1 (t, $^1J_{CP}$ = 8.9 Hz, PMe$_3$); ^{31}P{^{1}H} NMR (toluene-d_8, −80 °C) δ −19 (br s).

Preparation of $Ta(C_2H_4)(OCMe_3)_2(PMe_3)_2Cl$. $Ta(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ (0.26 g, 0.51 mmol), PMe_3 (0.080 g, 1.0 mmol), and

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[21] (a) An analogous complex, $NbCl_3(PPhMe_2)_2$, has been prepared by Riess.[21b] (b) Hubert-Pfalzgraf, L.; Riess, J. G. *Inorg. Chim. Acta* **1978**, *29*, L251–252.

ether (5 mL) were placed in a pressure bottle and treated with ethylene (30 psi) for 4 h. Removing the solvent gave the yellow product quantitatively. It can be recrystallized in high yield from ether at −30 °C. Without added $\mathrm{PMe_3}$, $\mathrm{Ta(CHCMe_3)(OCMe_3)_2(PMe_3)Cl}$ gives 0.5 equiv of $\mathrm{Ta(C_2H_4)(OCMe_3)_2(PMe_3)_2Cl}$; the other product(s) could not be identified: ^{1}H NMR ($\mathrm{C_6D_6}$) δ 1.45 (m, 22, $\mathrm{PMe_3}$ and $\mathrm{C_2H_4}$), 0.82 (s, 18, $\mathrm{OCMe_3}$); ^{13}C NMR ($\mathrm{C_6D_6}$) δ 76.9 (s, $\mathrm{O}\mathit{C}\mathrm{Me_3}$), 38.7 (t, J_{CH} = 149 Hz, $\mathrm{C_2H_4}$), 21.7 (q, J_{CH} = 125 Hz, $\mathrm{OC}\mathit{Me}_3$), 15.0 (qt, J_{CH} = 127 Hz, J_{CP} = 10 Hz, $\mathrm{PMe_3}$).

Preparation of $\mathbf{Nb(C_2H_4)(OCMe_3)_2(PMe_3)_2Cl}$. A solution of $\mathrm{Nb(CHCMe_3)(OCMe_3)_2(PMe_3)_2Cl}$ (0.76 g, 1.81 mmol) in toluene (7 mL) containing $\mathrm{PMe_3}$ (0.3 g, 3.9 mmol, excess) was treated with 30 psi of ethylene for 6 h at 25 °C. The solution was filtered and stripped to orange residue which was extracted with pentane (~125 mL). The solution was filtered, and its volume was reduced (in vacuo) to 40 mL. Filtration gave 0.62 g (91% yield) of a microcrystalline product. An analytical sample was obtained by fractional crystallization from toluene/ether solutions: ^{1}H NMR (toluene-d_8, 270 MHz, −50 °C) δ 1.700 (m, 4, $\mathrm{C_2H_4}$), 1.311 (t, 18, $^2J_{\mathrm{HP}}$ = 3.1 Hz, $\mathrm{PMe_3}$), 0.816 (s, 18, $\mathrm{OCMe_3}$); ^{13}C{^{1}H} NMR (toluene-$\mathrm{D_8}$, −20 °C) δ 76.4 (s, $\mathrm{O}\mathit{C}\mathrm{Me_3}$), 42.4 (br s, $\mathrm{C_2H_4}$), 31.29 (s, $\mathrm{OC}\mathit{Me}_3$), 14.83 (br, $\mathrm{PMe_3}$).

Anal. Calcd for $\mathrm{NbC_{16}H_{40}O_2ClP_2}$: C, 42.26; H, 8.87. Found: C, 41.85; H, 8.63.

Preparation of $\mathbf{Ta(CHC_6H_5)(OCMe_3)_2(PMe_3)_2Cl}$ from $\mathbf{Ta(CHCMe_3)(OCMe_3)_2(PMe_3)_2Cl}$ and Styrene. $\mathrm{Ta(CHCMe_3)(OCMe_3)_2(PMe_3)Cl}$ (2.0 g, 3.93 mmol) was dissolved in toluene (10 mL) containing 0.5 mL of $\mathrm{PMe_3}$. Styrene (0.50 g, 4.75 mmol) in 2 mL of toluene was added. After 2 min the color changed from yellow to orange, and after 1.5 h it changed to green. The reaction mixture was cooled to −30 °C for 12 h, and green flakes (1.21 g) were isolated by filtration. The mother liquor was stripped, and the residue was dissolved in 5 mL of toluene which contained 0.2 mL of $\mathrm{PMe_3}$. After 12 h at −30 °C an additional 0.6 g of product was isolated; total yield 76%; ^{1}H NMR (toluene-d_8, 270 MHz) δ 9.963 (t, 1, $^3J_{\mathrm{HP}}$ = 3.8 Hz, $\mathrm{C}\mathit{H}\mathrm{C_6H_5}$), 7.32, 7.05, 6.72 (m, ~5, aromatic H), 1.589 (s, 9, $\mathrm{OCMe_3}$), 1.499 (s, 9, $\mathrm{OCMe_3'}$), 1.085 (t, 18, $^2J_{\mathrm{HP}}$ = 3.1 Hz, $\mathrm{PMe_3}$); ^{13}C{^{1}H} NMR (THF-d_8) δ 258 (br, $\mathit{C}\mathrm{HC_6H_5}$), 138 (br, $\mathrm{C_{ipso}}$), 129, 128, 127 ($\mathrm{C_o}$, $\mathrm{C_m}$, $\mathrm{C_p}$), 80.8 (s, $\mathrm{O}\mathit{C}\mathrm{Me_3}$), 79.9 (s, $\mathrm{O}\mathit{C}\mathrm{Me_3'}$), 33.2 (s, $\mathrm{OC}\mathit{Me}_3$), 32.4 (s, $\mathrm{OC}\mathit{Me}_3'$), 15.6 (t, $^1J_{\mathrm{CP}}$ = 11 Hz, $\mathrm{PMe_3}$).

Observation of $\mathbf{[Ta(CHC_6H_5)(OCMe_3)_2(PMe_3)Cl]_x}$ (x = 1 or 2). $\mathrm{Ta(CHCMe_3)(OCMe_3)_2(PMe_3)Cl}$ (2.10 g, 4.13 mmol) in ether (35 mL) reacted immediately with styrene (0.55 g, 5.28 mmol) at 25 °C. In 10 min a small amount of orange solid precipitated from solution. The solvent was removed in vacuo, leaving an oily solid which was triturated with ether, leaving 0.44 g of a yellow powder; yield 20%. By ^{1}H NMR it is a mixture of ~80% $\mathrm{Ta(CHC_6H_5)(OCMe_3)_2(PMe_3)Cl}$ and ~20% $\mathrm{Ta(CHC_6H_5)(OCMe_3)_2(PMe_3)_2Cl}$. Similar results were obtained when *cis*-stilbene was used in place of styrene, but the sample could not be freed of *trans*-stilbene mixtures of the monophosphine and bisphosphine complexes were also obtained by exposing a toluene solution containing $\mathrm{Ta(CHC_6H_5)(OCMe_3)_2(PMe_3)_2Cl}$ or the crystalline solid to a moderate vacuum. Attempts to prepare pure $\mathrm{Ta(CHC_6H_5)(OCMe_3)_2(PMe_3)Cl}$ were unsuccessful due to its ready decomposition: ^{1}H NMR (toluene-d_8, 270 MHz, −40 and 30 °C) δ 10.44 (d, 1, $^3J_{\mathrm{HP}}$ = 3.6 Hz, $\mathrm{C}\mathit{H}\mathrm{C_6H_5}$), 7.27, 7.13, 6.74 (m, 5, aromatic H), 1.406 (s, 9, $\mathrm{OCMe_3}$), 1.394 (s, 9, $\mathrm{OCMe_3'}$), 0.813 (d, 9, $^2J_{\mathrm{HP}}$ = 7.9 Hz, $\mathrm{PMe_3}$); ^{13}C{^{1}H} NMR (THF-d_8, 5 °C) δ 257 (br, $\mathit{C}\mathrm{HC_6H_5}$), 145 (br, $\mathrm{C_{ipso}}$), 129, 127, 125 ($\mathrm{C_o}$, $\mathrm{C_m}$, $\mathrm{C_p}$), 81.8 (s, $\mathrm{O}\mathit{C}\mathrm{Me_3}$), 80.9 (s, $\mathrm{O}\mathit{C}\mathrm{Me_3'}$), 32.2 (br, $\mathrm{OC}\mathit{Me}_3$), 15.5 (d, $^1J_{\mathrm{CP}}$ = 25 Hz, $\mathrm{PMe_3}$).

Reaction of $\mathbf{Nb(CHCMe_3)(OCMe_3)_2(PMe_3)Cl}$ with Styrene in the Presence of $\mathbf{PMe_3}$. $\mathrm{Nb(CHCMe_3)(OCMe_3)_2(PMe_3)Cl}$ (0.42 g, 1.0 mmol) was dissolved in toluene (8 mL) containing 0.080 g of $\mathrm{PMe_3}$, and the solution was cooled to −30 °C. Styrene (0.11 g, 1.06 mmol, 6% excess) in 2 mL of toluene was added dropwise to the stirred solution. The reaction mixture was warmed to 25 °C and stirred for 2 h. Pentane (~15 mL) was added to the reaction mixture. Orange crystals were filtered off after 40 h at −30 °C; yield 0.44 g. The orange crystals were shown to be a 2:1 mixture of $\mathrm{Nb(CHC_6H_5)(OCMe_3)_2(PMe_3)_2Cl}$ and $\mathrm{Nb(CHC_6H_5)(OCMe_3)_2(PMe_3)Cl}$ by ^{1}H NMR; ^{1}H NMR (toluene-d_8, 250 MHz, −30 °C) [$\mathrm{Nb(CHC_6H_5)(OCMe_3)_2(PMe_3)Cl}$] δ 12.410 (d, 1, $^3J_{\mathrm{HP}}$ = 4.4 Hz, $\mathrm{C}\mathit{H}\mathrm{C_6H_5}$), 7.47, 7.18, 6.85 (m, aromatic H), 1.596 (s, 9, $\mathrm{OCMe_3}$), 1.532 (s, 9, $\mathrm{OCMe_3'}$), 0.729 (d, 9, $^2J_{\mathrm{HP}}$ = 7.4 Hz, $\mathrm{PMe_3}$), [$\mathrm{Nb(CHC_6H_5)(OCMe_3)_2(PMe_3)_2Cl}$] δ 12.086 (t, 1, $^3J_{\mathrm{HP}}$ = 4.4 Hz, $\mathrm{C}\mathit{H}\mathrm{C_6H_5}$), 7.47, 7.18, 6.85 (m, aromatic H), 1.449 (s, 9, $\mathrm{OCMe_3}$), 1.414 (s, 9, $\mathrm{OCMe_3'}$), 1.020 (t, 18, $^2J_{\mathrm{HP}}$ = 2.9 Hz, $\mathrm{PMe_3}$).

Preparation of $\mathbf{Ta(CHCMe_3)(OCMe_3)_3}$. $\mathrm{Ta(CHCMe_3)(THF)_2Cl_3}$ (3.0 g, 6.0 mmol) was dissolved in 25 mL of ether and cooled to −20 °C. A cold solution of $\mathrm{LiOCMe_3}$ (1.44 g, 17.9 mmol) in ether was added while the mixture was being stirred. The reaction immediately turned orange, and after about 1 h, it turned yellow. After the solution was stirred for 8 h the LiCl was filtered off and the ether removed in vacuo to yield an orange oil; ^{13}C NMR ($\mathrm{C_6D_6}$): δ 210.2 (d, J_{CH} = 96 Hz, $\mathit{C}\mathrm{HCMe_3}$), 78.1 ($\mathrm{O}\mathit{C}\mathrm{Me_3}$), 42.2 (s, $\mathrm{CH}\mathit{C}\mathrm{Me_3}$), 36.6 (q, J_{CH} = 125 Hz, $\mathrm{CHC}\mathit{Me}_3$), 32.3 (q, J_{CH} = 125, $\mathrm{OC}\mathit{Me}_3$).

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