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Tungsten(VI) Neopentylidyne Complexes[†,1]

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Tungsten hexachloride reacts with 6 equiv of neopentyllithium in ether to give volatile, yellow, crystalline $W(CCMe_3)Np_3$ ($Np = CH_2CMe_3$) in poor yield. $W(CCMe_3)Np_3$ can be prepared in 50–70% yield by adding $W(OMe)_3Cl_3$ to 6 equiv of NpMgCl in ether. $W(CCMe_3)Np_3$ reacts with 3 equiv of HCl in the presence of NEt_4Cl to give blue $[NEt_4][W(CCMe_3)Cl_4]$ and in the presence of dme to give $W(CCMe_3)(dme)Cl_3$ (dme = 1,2-dimethoxyethane). The several phosphine adducts of "$W(CCMe_3)Cl_3$" which have been prepared include $W(CCMe_3)(L)Cl_3$ ($L = PEt_3$ or PMe_3), $W(CCMe_3)(PMe_3)_2Cl_3$, and $W(CCMe_3)(PMe_3)_3Cl_3$. Straightforward reactions between $[NEt_4]$ or $W(CCMe_3)(dme)Cl_3$ and LiX ($X = OCMe_3$, NMe_2, N-*i*-Pr_2, or $SCMe_3$) give the volatile, pale yellow to white, monomeric complexes, $W(CCMe_3)X_3$.

Introduction

Several years ago we discovered that the reaction between WCl_6 and 6 equiv of neopentyllithium in diethyl ether produces the volatile yellow neopentylidyne complex, $W(CCMe_3)(CH_2CMe_3)_3$, in low yield.[2] We were able to study some of its reactions, such as that with phosphine ligands to give complexes of the type $W(CCMe_3)(CHCMe_3)(CH_2CMe_3)L_2$ ($L = PMe_3$ or 0.5 dmpe),[2,3] but the chemistry of what we suspected might be an important type of tungsten(VI) organometallic species (viewing the neopentylidyne ligand as a trianion analogous to the nitride ligand[4]) unfortunately was limited by the low-yield route to $W(CCMe_3)(CH_2CMe_3)_3$ and our failure to find a route to versatile derivatives. The picture changed in 1981 when we discovered $[W(CCMe_3)Cl_4]^-$ via an unexpected route,[5] a route to $W(CCMe_3)(CH_2CMe_3)_3$ in good yield on a relatively large scale,[6] and the reaction between $W(CCMe_3)(CH_2CMe_3)_3$ and 3 equiv of HCl in the presence of NEt_4Cl to give $[NEt_4][W(CCMe_3)Cl_4]$ essentially quantitatively.[6] From $[NEt_4][W(CCMe_3)Cl_4]$ we could not only prepare a variety of adducts of the type $W(CCMe_3)Cl_3L_x$ (x = 1, 2, or 3) where L = (e.g.) PR_3 but also, more interestingly, a variety of simple thermally stable molecules of the type $W(CCMe_3)X_3$ ($X = OCMe_3$, $SCMe_3$, NR_2). The details of this chemistry are reported in this paper. Reactions of tungsten(VI) neopentylidyne complexes, including their use as catalysts to catalytically metathesize acetylenes,[7] will be reported in detail in subsequent papers.

Results

Preparation of $W(CCMe_3)(CH_2CMe_3)_3$. Yellow, crystalline $W(CCMe_3)Np_3$ ($Np = CH_2CMe_3$) was first prepared in low yield by adding 6 equiv of LiNp to WCl_6 in ether at −78 °C, followed by warming the yellow solution to room temperature, removing the solvent in vacuo, and subliming the pentane-soluble residues (70 °C (1 μm)). Ether apparently is necessary since if >50% of the solvent is pentane, little or no $W(CCMe_3)Np_3$ can be isolated. $W(CCMe_3)Np_3$ can also be prepared by adding 5 equiv of LiNp to WCl_5 in ether at −78 °C (followed by a similar isolation procedure) or 6 equiv of LiNp to WBr_6. The yield of $W(CCMe_3)Np_3$ from WCl_6 and LiNp was unchanged by employing inverse addition (W to Li) or by doing the reaction at room temperature. Using NpMgCl in place of LiNp gave only traces of $W(CCMe_3)Np_3$, if any at all.

Table I. Some ^{13}C NMR Data for Tungsten(VI) Neopentylidyne Complexes

compd	solvent	$\delta(C_\alpha)$	J_{CW}	J_{CP}
$W(CCMe_3)Np_3$	C_6D_6	316	232	
$W(CCMe_3)(OCMe_3)_3$	$CDCl_3$	271		
$W(CCMe_3)(NMe_2)_3$	C_6D_6	288		
$W(CCMe_3)(SCMe_3)_3$	$CDCl_3$	335		
$[W(CCMe_3)(OMe)_3(NMe_2H)]_2$	C_6D_6	286		
$[PEt_3H][W(CCMe_3)Cl_4]$	CD_2Cl_2	339	205	
$[NEt_4][W(CCMe_3)Cl_4]$	CD_2Cl_2	337		
$[NEt_4][W(CCMe_3)(PEt_3)Cl_4]$	$CDCl_3$	335		13
$W(CCMe_3)(dme)Cl_3$	C_6D_6	335	224	
$W(CCMe_3)(Et_3PO)Cl_3$	C_6D_6	329	208	
$W(CCMe_3)(Et_3PO)(PEt_3)Cl_3$	C_6D_6	340		15
$W(CCMe_3)(PMe_3)_3Cl_3$	$CDCl_3$	401		40
$W(CCMe_3)(PMe_3)_2Cl_3$	$CDCl_3$	357		26
$W(CCMe_3)(PMe_3)Cl_3$	$CDCl_3$	345		12
$W(CCMe_3)(PEt_3)Cl_3$	C_6D_6	346	209	13

The mass spectrum of $W(CCMe_3)Np_3$ shows a correct isotope pattern for the $W(CCMe_3)Np_3^+$ ion. No higher mass peaks were found. Since $W(CCMe_3)Np_3$ is extremely soluble in pentane, toluene, and ether, one might suspect that it is monomeric. Although a cryoscopic molecular weight measurement in cyclohexane suggested that it might be a dimer,[2] more reliable differential vapor-pressure studies in dichloromethane (at 0 °C) confirm that it is a monomer.

The ^1H and ^{13}C NMR spectra of $W(CCMe_3)Np_3$ are consistent with its formulation. The signal for the neopentylidyne α-carbon atom is found at 316 ppm with J_{CW} = 232 Hz, data which suggest there is a triple bond between tungsten and carbon.[2,3] ^{13}C NMR data for this and other neopentylidyne complexes we will be discussing are collected in Table I.

The IR spectrum of $W(CCMe_3)Np_3$ is very similar to that of $Ta(CHCMe_3)Np_3$,[8] the major differences being in the fingerprint region. Some of these could be due to a

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[†] This paper is dedicated to the memory of Rowland Pettit, a brilliant chemist and a friend. Pettit was one of the first to attempt to prepare a complex containing a terminal methylene ligand, and he took a special interest in the emerging area of high oxidation state complexes containing a metal–carbon double or triple bond.

(1) Multiple Metal–Carbon Bonds. 31. For part 30 see: Edwards, D. S.; Schrock, R. R. *J. Am. Chem. Soc.*, in press.

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(6) Sancho, J. Ph.D. Thesis, Massachusetts Institute of Technology, 1982.

(7) (a) Wengrovius, J. H.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 3932. (b) Sancho, J.; Schrock, R. R. *J. Mol. Catal.* **1982**, *15*, 75.

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

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"M≡C" stretching mode (e.g., at 1350 or 1280 cm^{-1} for $W(CCMe_3)Np_3$) analogous to those assigned by Fischer in a series of $X(CO)_4W{\equiv}CR$ complexes,[9] but careful studies are clearly necessary before reaching any conclusions.

Although WMe_6 is known,[10] it seemed unlikely to us that $W(CH_2CMe_3)_6$ was an intermediate in the reaction to give $W(CCMe_3)Np_3$ by a double intramolecular α-hydrogen atom abstraction reaction,[11] i.e., $W(CH_2CMe_3)_6 \rightarrow W(CHCMe_3)(CH_2CMe_3)_4 \rightarrow W(CCMe_3)(CH_2CMe_3)_3$. The reason is that WCl_6 is extremely easy to reduce and only use of the mildest alkylating agents (for example, mercury alkyls[12]) can prevent reduction.[13] Indeed, analysis of the volatile components from a typical reaction showed that from 3.2 to 3.5 equiv of added neopentyl groups are found as neopentane (~1.3 equiv) and 2,2,4,4-tetramethylhexane (~1.0 equiv). Therefore it appeared likely that much of the neopentyllithium was consumed as a reducing agent.

Closer examination confirmed that only 4 equiv of LiNp are required to produce a yellow solution at −78 °C. When the volatile components were removed at −78 °C from a yellow solution prepared in this manner, they were found to include ~2.7 equiv of C_5 products (~0.9 equiv of neopentane and ~0.9 equiv of dineopentyl); i.e., the first three equivalents of neopentyllithium simply reduce W(VI) to W(III) (eq 1). The fourth equivalent of neopentyllithium

$$WCl_6 + 4LiNp \rightarrow CMe_4 + Me_3CCH_2CH_2CMe_3 + \text{“}WNpCl_2\text{”} \quad (1)$$

probably alkylates "WCl_3" to give "$WNpCl_2$", the yellow powder that is left behind in this experiment. When fresh ether is added to "$WNpCl_2$" at −78 °C and the solution is allowed to warm to 25 °C, an ugly brown mixture is formed from which neopentane (0.12 equiv) and dineopentyl (0.33 equiv) can be removed in vacuo at 25 °C.

In another set of experiments 6 equiv of neopentyllithium were added to WCl_6, and all volatile components were removed at −30 °C, leaving a yellow residue. We could not extract any unreacted neopentyllithium from this residue with hexane at −30 °C. Therefore we suggest that "$WNpCl_2$" is further alkylated to "WNp_2Cl" and finally "WNp_3" and that "WNp_3" decomposes between ~0 and 20 °C to give (inter alia) $W(CCMe_3)Np_3$. We believe that some neopentane is formed when "WNp_3" decomposes, since we know that ~1.3 equiv of neopentane and ~1.0 equiv of dineopentyl are found at the end of a typical preparation of $W(CCMe_3)Np_3$ from WCl_6 and LiNp, but only ~1.0 equiv of neopentane and ~1.0 equiv of dineopentyl are formed in the first three reduction steps (see above). If we could be certain that no dineopentyl forms when "WNp_3" decomposes (even though dineopentyl forms when "$WNpCl_2$" decomposes), then we could be fairly certain that the final series of steps to give $W(CCMe_3)Np_3$ results in formation only of neopentane, probably via complex α-hydrogen abstraction reactions. We feel this is probably true but cannot prove it due to the experimental errors involved.

It should be clear by now that the preparation of $W(CCMe_3)Np_3$ from WCl_6 and LiNp is complex, probably involving electron transfers, intermolecular α-hydrogen abstractions, alkyl transfers, disproportionations, etc. The low yield might be tolerable were it not for the fact that the yield is even lower when the reaction is scaled up by a factor of 5. Therefore we had to develop an alternative synthesis of $W(CCMe_3)Np_3$. We hypothesized that it would be preferable to keep the tungsten from reducing in order that a relatively well-behaved double α-hydrogen abstracting reaction to yield a W(VI) neopentylidyne complex would be possible. Initial attempts at preparing $W(CCMe_3)Np_3$ from $WOCl_4$, WO_2Cl_2, or $WO(OCMe_3)_4$ plus 6 equiv of LiNp, NpMgCl, or $MgNp_2$ in ether or pentane by using both regular and inverse addition (W to alkylating agent) at −78 °C or 25 °C gave no better yields of $W(CCMe_3)Np_3$ (if any at all) than from WCl_6 and LiNp. We then turned to methoxy chloride complexes since methoxide ligands should make the metal less susceptible to reduction and since methoxide ligands should be substituted readily by alkylating agents.

$W(OMe)_3Cl_3$ and $W(OMe)_4Cl_2$ are readily prepared in high yield from WCl_6 and Me_3SiOMe.[14] When up to 6 equiv of LiNp or NpMgCl or 3 equiv of $ZnNp_2$ are added to $W(OMe)_3Cl_2$ or $W(OMe)_4Cl_2$ in ether or pentane, only unidentifiable, essentially insoluble precipitates and/or pentane-soluble red oils were obtained. Little or no $W(CCMe_3)Np_3$ could be sublimed from the red oils. However, when $W(OMe_3)_3Cl_3$ is added *to* 6 equiv of NpMgCl in ether at −78 °C, followed by warming the reaction to room temperature and working it up as before, a large amount of pentane-soluble red oil is obtained in which the only significant diamagnetic product is $W(CCMe_3)Np_3$. $W(CCMe_3)Np_3$ can be *distilled* in 50–70% yield from this red oil at 80–90 °C and 0.1–1 μm of pressure by using a short-path, air-cooled distillation head. Since $W(OMe)_3Cl_3$ can be prepared in high yield on a large scale and since the alkylation reaction can be run conveniently by using 20–40 g of $W(OMe)_3Cl_3$, this procedure immediately superceded the preparation of $W(CCMe_3)Np_3$ from WCl_6 using LiNp. We believe that methoxide ligands prevent reduction of the metal before an α-hydrogen atom abstraction reaction[11,15] can produce a neopentylidene ligand. Once the initial neopentylidene ligand forms, the remaining α-hydrogen atom is probably relatively easily removed by an alkyl group or even a methoxide or a chloride ligand. We hope to be able to investigate the mechanism of this reaction in the future.

The Preparation of $[W(CCMe_3)Cl_4]^-$ and Related Species. The first evidence that neopentylidyne complexes probably are common and readily formed was uncovered in the study of tungsten(VI) oxo neopentylidene complexes.[16] The reaction shown in eq 2 was an attempt

$$W(O)(CHCMe_3)(PEt_3)_2Cl_2 \xrightarrow[-C_2Cl_4]{C_2Cl_6,\ \text{chlorobenzene}} Et_3PO + [PEt_3][W(CCMe_3)Cl_4] \quad (2)$$

to prepare the known[16] five-coordinate species, $W(O)(CHCMe_3)(PEt_3)Cl_2$, by oxidizing one relatively labile phosphine ligand to PEt_3Cl_2.[17] In tetrahydrofuran the

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(9) Fischer, E. O.; Dao, N. Q.; Wagner, W. R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 50.

(10) Chiu, K. W.; Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1981**, 1204–1211 and references therein.

(11) (a) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98. (b) Schrock, R. R. "Alkylidene Complexes of the Earlier Transition Metals" in "Reactions of Coordinated Ligands"; Braterman, P. S., Ed.; Plenum Press: New York, in press.

(12) Riess has reported preparing $WMeCl_5$ from WCl_6 and $HgMe_2$: Santini-Scampucci, C.; Riess, J. G. *J. Chem. Soc., Dalton Trans.* **1976**, 195. We attempted to prepare "$WNpCl_5$" by reacting $HgNp_2$ with WCl_6 at low temperatures in CH_2Cl_2. A reaction does occur but we have been unable to determine what the tungsten product(s) is (are) or to convert them into any recognizable derivative.

(13) However, the latest and most successful preparation of WMe_6[10] employs $AlMe_3$, apparently without any complications which could be ascribed to significant reduction of the tungsten.

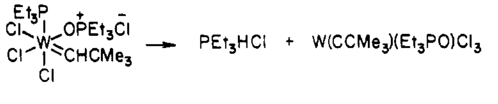
(14) Handy, L. B.; Sharp, K. G.; Brinckman, F. F. *Inorg. Chem.* **1972**, *11*, 523.

(15) (a) Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210. (b) Messerle, L. W.; Jennische, P.; Schrock, R. R.; Stucky, G. D. *Ibid.* **1980**, *102*, 6744.

(16) Wengrovius, J. H.; Schrock, R. R. *Organometallics* **1982**, *1*, 148.

reaction proceeds differently (eq 3). $[PEt_3H][W(CCMe_3)Cl_4]$ is easily isolated as blue crystals. Unfortunately, $W(CCMe_3)(Et_3PO)Cl_3$ could be obtained only as a blue oil. In each case the first step is probably oxidation of one dissociated PEt_3 ligand in $W(O)(CHCMe_3)(PEt_3)_2Cl_2$ to PEt_3Cl_2. We propose that the phosphorus(V) in PEt_3Cl_2 attacks the oxo ligand in $W(O)(CHCMe_3)(PEt_3)Cl_2$ to give an intermediate which is perhaps that shown in eq 4. Apparently this renders the neopentylidene α-proton relatively acidic (see later), and it is then removed by PEt_3 to give PEt_3HCl. This proposal is supported by the fact that authentic $W(O)(CHCMe_3)(PEt_3)Cl_2$ reacts with PPr_3Cl_2 in THF more rapidly than the rate of reaction 3 to give the result shown in eq 5 (Pr = *n*-propyl). One final piece of (negative) evidence consistent with the proposed mechanism is the fact that $W(O)(CHCMe_3)(PEt_3)Cl_2$ does not react readily with C_2Cl_6.

$$W(O)(CHCMe_3)(PEt_3)_2Cl_2 \xrightarrow[-C_2Cl_4]{C_2Cl_6,\ THF} PEt_3HCl + W(CCMe_3)(Et_3PO)Cl_3 \quad (3)$$



(4)

$$W(O)(CHCMe_3)(PEt_3)_2Cl_2 + PPr_3Cl_2 \rightarrow PEt_3HCl + W(CCMe_3)(Pr_3PO)Cl_3 \quad (5)$$

We soon realized that $[W(CCMe_3)Cl_4]^-$ might be prepared independently by adding HCl to $W(CCMe_3)Np_3$ in the presence of NEt_4Cl. This reaction (eq 6) works well in a mixture of ether and dichloromethane. Yields of $[NEt_4][W(CCMe_3)Cl_4]$ are consistently >90%. A small amount of an unidentified red impurity occasionally forms, but it can be separated from the product easily. Surprisingly, excess HCl does not react readily with $[NEt_4][W(CCMe_3)Cl_4]$. Therefore, we can propose that $W(CHCMe_3)Cl_4$, if it were formed via some other route, almost certainly would immediately lose H^+ to give $[W(CCMe_3)Cl_4]^-$ or HCl to give "$W(CCMe_3)Cl_3$" (see below).

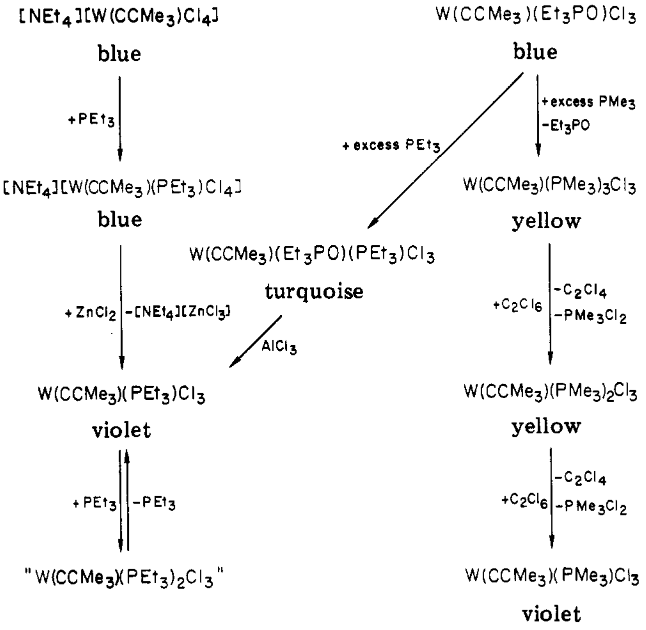
$$W(CCMe_3)(CH_2CMe_3)_3 \xrightarrow[NEt_4Cl]{3HCl} [NEt_4][W(CCMe_3)Cl_4] \quad (6)$$

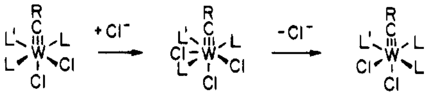
If NEt_4Cl is left out of the reaction of $W(CCMe_3)Np_3$ with 3 equiv of HCl in ether (for example), a poorly behaved and as yet uncharacterized green powder is obtained. The green powder dissolves in THF, but no well-behaved compound could be isolated. ^1H and ^{13}C NMR spectra of solutions of "$W(CCMe_3)Cl_3$" in THF were broad and variable, as if paramagnetic impurities were present. However, a well-behaved 1,2-dimethoxyethane adduct can be obtained by reacting $W(CCMe_3)Np_3$ in pentane with HCl in the presence of dimethoxyethane (eq 7). $W(CCMe_3)(dme)Cl_3$ is a purple, crystalline complex whose ^1H and ^{13}C NMR spectra suggest that it is octahedral with three chloride ligands cis to the neopentylidyne ligand.

$$W(CCMe_3)Np_3 \xrightarrow[pentane,dme]{3HCl} W(CCMe_3)(dme)Cl_3 \quad (7)$$

It should be possible to form a large variety of adducts of "$W(CCMe_3)Cl_3$". We have already mentioned $W(CCMe_3)(dme)Cl_3$ and $W(CCMe_3)(Et_3PO)Cl_3$. It was initially for the purpose of confirming that Et_3PO was present in the latter that we reacted $W(CCMe_3)(Et_3PO)Cl_3$ with excess PEt_3 and PMe_3. As shown in Scheme I, these reactions yield $W(CCMe_3)(Et_3PO)(PEt_3)Cl_3$ and $W(CCMe_3)(PMe_3)_3Cl_3$, respectively. Two isomers of $W(CCMe_3)(Et_3PO)(PEt_3)Cl_3$ are observed, and in each the signal for the alkylidyne α-carbon atom is a doublet with J_{CP} = 14.5 Hz. Therefore, PEt_3 must be cis to the neopentylidyne ligand in each. $W(CCMe_3)(PMe_3)_3Cl_3$ is a peculiar species which is moderately soluble in toluene but also conducts slightly in dichloromethane. All PMe_3 ligands are equivalent and remain bound to tungsten (J_{PW} = 247 Hz and $J_{C_\alpha W}$ = 40 Hz) in either chloroform or toluene. We suspect that neutral, seven-coordinate $W(CCMe_3)(PMe_3)_3Cl_3$ is in rapid equilibrium with $[W(CCMe_3)(PMe_3)_3Cl_2]Cl$, even in toluene, and that the PMe_3 ligands equilibrate when chloride ligands exchange. One possible mechanism is shown in eq 8. We have not been able to slow down the chloride-exchange process on the NMR time scale by cooling samples to low temperatures.

Scheme I. Preparation of Some Phosphine Adducts





(8)

One PMe_3 ligand in $W(CCMe_3)(PMe_3)_3Cl_3$ can be oxidized with C_2Cl_6 to give $W(CCMe_3)(PMe_3)_2Cl_3$. The ^1H NMR spectrum of $W(CCMe_3)(PMe_3)_2Cl_3$ shows only one doublet for the PMe_3 ligands, not the "virtual triplet" characteristic of trans PMe_3 ligands. Therefore, we believe the two PMe_3 ligands are cis to one another and cis to the neopentylidyne ligand.

A second PMe_3 ligand can be oxidized with C_2Cl_6 to give violet $W(CCMe_3)(PMe_3)Cl_3$. An analogous violet PEt_3 complex was first made by treating $W(CCMe_3)(Et_3PO)(PEt_3)Cl_3$ with $AlCl_3$. In contrast to $W(CCMe_3)(PMe_3)_2Cl_3$, $W(CCMe_3)(PEt_3)_2Cl_3$ is not a stable species, although it is the likely intermediate which serves to exchange coordinated PEt_3 in $W(CCMe_3)(PEt_3)Cl_3$ with free PEt_3.

The majority of these results can be explained largely on the basis of the somewhat smaller size of PMe_3 relative to PEt_3. All of the phosphine complexes have been prepared more straightforwardly from $[Et_4N][W(CCMe_3)Cl_4]$ in the presence of $ZnCl_2$ (to remove Cl^- as NEt_4ZnCl_3), and we have shown in qualitative reactions that several of the

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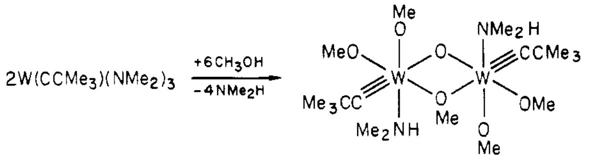
(17) Apel, R.; Schöler, H. *Chem. Ber.* **1977**, *110*, 2382.

phosphine complexes can be prepared from the most recently discovered complex, $W(CCMe_3)(dme)Cl_3$. Presumably all (and potentially a large variety of other types of adducts) could be prepared simply and quantitatively from $W(CCMe_3)(dme)Cl_3$.

Preparation of Complexes of the Type $W(CCMe_3)X_3$ ($X = OCMe_3, NR_2, SCMe_3$). $[NEt_4][W(CCMe_3)Cl_4]$ reacts with LiX ($X = OCMe_3$, NMe_2, N-*i*-Pr_2, or $SCMe_3$) to give pale yellow to white, volatile, monomeric species whose physical properties resemble those of $W(CCMe_3)Np_3$. Presumably these molecules cannot dimerize through $OCMe_3$, NR_2, or $SCMe_3$ bridges largely for steric reasons. Since the dimethylamido group is almost certainly planar and by analogy with the structure of $W_2(NMe_2)_6$,[18] one might expect to find the planes in which the dimethylamido ligands lie in $W(CCMe_3)(NMe_2)_3$ to contain the $W{\equiv}C$ bond. But at room temperature only one type of methyl group is observed, probably due to rotation of the dimethylamido ligand about the tungsten–nitrogen bond. In $W(CCMe_3)(N\text{-}i\text{-}Pr_2)_3$, however, a sterically more congested molecule in which rotation of the N-*i*-Pr_2 ligand about the tungsten–nitrogen bond should be slower, two types of methyl groups are observed in the NMR spectra. We assume one type is in an isopropyl group that points toward the neopentyl ligand and the other is in an isopropyl group that points away from the neopentylidyne ligand.

The importance of steric hindrance in keeping these molecules monomeric becomes obvious if one attempts to prepare analogous species in which X is a smaller ligand. For example, $W(CCMe_3)(NMe_2)_3$ reacts instantly with methanol to give $[W(CCMe_3)(OMe)_3(NMe_2H)]_2$. Its NMR spectra show three different types of methoxide ligands in a 1:1:1 ratio and a normal neopentylidyne ligand. A logical and consistent structure is that shown in eq 9. The metal is obviously still electrophilic enough to accept as many donor ligands as is sterically possible, even though the terminal alkoxide ligands are reasonably good π-electron donors.[19] The consequences of this behavior will become important in any reaction in which the substrate (e.g., an acetylene[7]) must coordinate to the metal. It is interesting to note in this context that $W_2(NMe_2)_6$ reacts with *tert*-butyl alcohol to give $W_2(OCMe_3)_6$, but the product of the reaction between $W_2(NMe_2)_6$ and Me_3SiOH is $W_2(OSiMe_3)_6(HNMe_2)_2$, and the products of the reaction between $W_2(NMe_2)_6$ and 2-propanol are polynuclear ($W > 2$).[20]



Discussion

Reactions between WCl_6 and several alkylating agents have been studied in the past.[21] All are complex. For example, the original preparation of WMe_6[10] was successful only when molecular oxygen was judiciously added. Possibly oxygen was required in order to oxidize some intermediate reduced tungsten complex. The reactions between WCl_6 and ((trimethylsilyl)methyl)lithium or Grignard reagents have yielded $W_2(CH_2SiMe_3)_6$,[22] $[W_2(CSiMe_3)(CH_2SiMe_3)_2]_2$,[23] and $W(CSiMe_3)(CH_2SiMe_3)_3$,[24] the (trimethylsilyl)methyl analogue of $W(CCMe_3)(CH_2CMe_3)_3$, all in low and variable yield (<20%). Therefore it is not surprising that the reaction between WCl_6 and neopentyllithium gives $W(CCMe_3)(CH_2CMe_3)_3$ in poor yield or that other, as yet unidentified neopentyl-derived products are also formed in this complex reaction. On the basis of the results described here, it is also not surprising to find that $W(CSiMe_3)(CH_2SiMe_3)_3$ can be prepared in 70% yield by adding $W(OMe)_3Cl_3$ to 6 equiv of Me_3SiCH_2MgCl.[25] $W(CSiMe_3)(CH_2SiMe_3)_3$ is yellow, crystalline,[26] sublimable, and distillable. It and its reactions will be described fully in due course.

We recently reported some relatively well-behaved α-hydrogen abstraction reactions in tungsten imido neopentyl complexes which give imido neopentylidene complexes.[27] There are indications that tungsten oxo neopentyl complexes also undergo α-hydrogen abstraction reactions to give oxo neopentylidene complexes.[28] In each case a strong π-bonding ligand (imido or oxo) apparently stabilizes the metal toward reduction. Without the π-donor ligand reduction is a significant problem and complex, unpredictable, intermolecular α-hydrogen abstraction reactions therefore predominate. The fact that $W(CCMe_3)Np_3$ forms at all when "WNp_3" decomposes is remarkable.

Tungsten(VI) neopentylidyne complexes, and, as we now know, other types of alkylidyne complexes (e.g., benzylidyne,[7] butylidyne,[29] etc.), are obviously closely related to nitrido complexes.[4] However, an important difference between the nitride and the alkylidyne ligand is that the nitrido ligand can form adducts of the type $M{\equiv}N{\rightarrow}M'$ with few steric problems, while the alkylidyne ligand is restricted to forming sterically more crowded "adducts" with approximately a square MC_2M' arrangement.[23,30]

Experimental Section

All operations were performed under prepurified nitrogen or argon by using standard Schlenk techniques or a Vacuum Atmospheres HE 43-2 drybox system.

Commerical pentane and hexane (washed with 5% HNO_3/H_2SO_4 and dried over $CaCl_2$), reagent grade THF (dried over KOH), reagent grade toluene and anhydrous ether were distilled from dark purple sodium benzophenone ketyl under nitrogen. Reagent grade benzene, dichloromethane, chloroform, and acetonitrile were dried by passage through an activated alumina column and then thoroughly deaerated with a nitrogen stream. Other solvents used in small amounts were usually dried by storage over Linde 4A molecular sieves and deaerated with nitrogen.

WCl_6 (Sylvania) was used as received. $MeOSiMe_3$ was prepared from methanol and hexamethyldisilazane, and purified by dis-

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tillation (57 °C). $\mathrm{NEt_4Cl}$ was dehydrated in vacuo at 105 °C for 24 h. $\mathrm{LiOCMe_3}$ was prepared in pentane from butyllithium and *tert*-butyl alcohol and recrystallized from pentane. LiN-*i*-$\mathrm{Pr_2}$ was prepared from butyllithium and diisopropylamine (previously distilled from BaO) in hexane and was not further purified. $\mathrm{W(OMe)_3Cl_3}$,[14] $\mathrm{W(OMe)_4Cl_2}$,[14] $\mathrm{PEt_3Cl_2}$,[17] $\mathrm{PPr_3Cl_2}$,[17] and $\mathrm{Et_3PO}$[31] were prepared as reported in the literature.

Molecular weights were determined in dichloromethane at 0 °C by differential vapor pressure measurement. Elemental analysis (C, H, P, N) on samples oxidized with $\mathrm{V_2O_5}$ were performed by Schwartzkopf Microanalytical Laboratories.

^{13}C NMR spectra were run in the gated ^{1}H-decoupled mode in order to obtain CH coupling constants and in the broad-band ^{1}H-decoupled mode in order to obtain the CW and/or CP coupling constants.

Preparations. $\mathbf{W(CCMe_3)(CH_2CMe_3)_3}$. (i) From $\mathbf{WCl_6}$. To 2.00 g of $\mathrm{WCl_6}$ stirred at room temperature in 40 mL of ether was added dropwise a solution of 2.36 g (6 equiv) of $\mathrm{LiCH_2CMe_3}$ in 40 mL of ether. The solution changed from red black to clear yellow to black and LiCl precipitated. The solution was stirred for 15 min and filtered to remove LiCl (ca. 1.2 g). Ether was removed in vacuo, and the oily residue was extracted with hexane, filtered to remove insolubles (ca. 0.6 g), and stripped to a thick tar. The product was isolated by vacuum sublimation (50–70 °C (1 μm)) to yield 0.6 g (29%) of yellow crystals. Remaining nonvolatiles (at temperatures up to 200 °C) weighed ca. 0.8 g.

(ii) From $\mathbf{W(OMe)_3Cl_3}$. A solution of $\mathrm{W(OMe_3)_3Cl_3}$ (19.1 g, 50 mmol) in a mixture of THF and ether was added very slowly to a 1 M solution of MgNpCl (0.3 mol) in ether at −78 °C with vigorous stirring. The color of the solution gradually turned yellow-green. After the addition was complete, no significant amount of precipitate was apparent. The reaction mixture was allowed to warm slowly from −78 to 25 °C over a period of 10 h to give a red-brown solution and abundant precipitate. The reaction mixture was filtered through Celite, and the insolubles were extracted with ether. The solvent was removed from the filtrate in vacuo to give a thick red-brown oily liquid. After 2 h in vacuo 200 mL of pentane was added to the oily residue, and the mixture was filtered and the volatiles again were removed from the filtrate in vacuo. The resulting oily red liquid was distilled at ~80 °C and 1 μm through a short-path distillation apparatus using a heating tape to drive the compound up the vertical portion (~10 cm) of the apparatus; yield 55–60%. An additional 5–10% yield can usually be had by extracting the tarlike residue with pentane, filtering off the insolubles, removing the pentane in vacuo, and again distilling the residue as before. The total yield is 60–70% of yellow $\mathrm{W(CCMe_3)(CH_2CMe_3)_3}$: ^{1}H NMR ($\mathrm{C_6D_6}$) δ 1.66 (s, 9, $\mathrm{CCMe_3}$), 1.23 (s, 27, $\mathrm{CH_2C}Me_3$), 1.05 (s, 6, $\mathrm{C}H_2\mathrm{CMe_3}$); ^{13}C NMR ($\mathrm{C_6D_6}$) δ 316.2 (s, J_{CW} = 232 Hz, $C\mathrm{CMe_3}$), 103.4 (t, J_{CH} = 115 Hz, J_{CW} = 89 Hz, $C\mathrm{H_2CMe_3}$), 52.78 (s, J_{CW} = 47 Hz, $\mathrm{C}C\mathrm{Me_3}$), 37.20 (s, $\mathrm{CH_2}C\mathrm{Me_3}$), 34.56 (q, J_{CH} = 126 Hz, $\mathrm{CH_2C}Me_3$), 32.41 (q, J_{CH} = 123 Hz, $\mathrm{CC}Me_3$); M_r ($\mathrm{CH_2Cl_2}$, differential vapor pressure, 0 °C) Calcd 466, found 453 at 0.083 M. Anal. Calcd for $\mathrm{WC_{20}H_{42}}$: C, 51.51; H, 9.07. Found: C, 51.32; H, 8.90.

$\mathbf{[Et_4N][W(CCMe_3)Cl_4]}$. A 1 M solution of HCl in ether (30 mmol) was added to an equimolar mixture of $\mathrm{W(CCMe_3)Np_3}$ (4.67 g, 10 mmol) and $\mathrm{NEt_4Cl}$ (1.65 g, 10 mmol) in 20 mL of dichloromethane at 0 °C. The color changed from yellow to green to red as a blue precipitate of the product was formed. After 20 min, the ice bath was removed and the reaction mixture stirred at room temperature for another 30 min. Filtration gave 4.5 g (~90%) of essentially pure product, an analytical sample of which was obtained by recrystallization from dichloromethane: ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ 3.24 (br q, $\mathrm{NC}H_2\mathrm{CH_3}$), 1.34 (br t, $\mathrm{NCH_2C}H_3$), 1.23 (s, $\mathrm{CCMe_3}$); ^{13}C NMR ($\mathrm{CD_2Cl_2}$) δ 337 ($C\mathrm{CMe_3}$), 52.4 ($\mathrm{N}C\mathrm{H_2CH_3}$), 45.7 ($\mathrm{C}C\mathrm{Me_3}$), 33.5 ($\mathrm{CC}Me_3$), 7.19 ($\mathrm{NCH_2}C\mathrm{H_3}$). Anal. Calcd for $\mathrm{WC_{13}H_{29}Cl_4N}$: C, 29.84; H, 5.57. Found: C, 30.28; H, 5.69.

$\mathbf{[PEt_3H][W(CCMe_3)Cl_4]}$. A solution of $\mathrm{W(O)(CHCMe_3)Cl_2(PEt_3)_2}$ (0.60 g, 1.04 mmol) and hexachloroethane (0.49 g, 2.08 mmol) in 10 mL of chlorobenzene was stirred for 3 h. The color of the homogeneous solution changed from yellow to blue. Pentane (2 mL) was added, and the cloudy solution was cooled to −30 °C to induce crystallization of 0.41 g (77%) of blue prisms in two crops. This product can be recrystallized from dichloromethane by adding pentane: ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ 6.81 (br d, 1, J_{HP} = 497 Hz, PH), 2.31 (br m, 6, $\mathrm{PC}H_2\mathrm{CH_3}$), 1.35 (dt, 9, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 20 Hz, $\mathrm{PCH_2C}H_3$), 1.21 (s, 9, $\mathrm{CCMe_3}$); ^{13}C NMR ($\mathrm{CD_2Cl_2}$) δ 339 (s, J_{CW} = 205 Hz, $C\mathrm{CMe_3}$), 47.5 (s, $\mathrm{C}C\mathrm{Me_3}$), 34.2 (q, J_{CH} = 127 Hz, $\mathrm{CC}Me_3$), 10.6 (dt, J_{CH} = 130 Hz, J_{CP} = 46 Hz, $\mathrm{P}C\mathrm{H_2CH_3}$), 7.10 (q, J_{CH} = 127 Hz, $\mathrm{PCH_2}C\mathrm{H_3}$); ^{31}P NMR ($\mathrm{CD_2Cl_2}$) δ 18.8 (d, J_{PH} = 498 Hz); IR (Nujol) 2420 m cm^{-1} (ν_{PH}).

$\mathbf{[Et_4N][W(CCMe_3)(PEt_3)Cl_4]}$. $\mathrm{PEt_3}$ (0.47 g, 4.0 mmol) was added to $\mathrm{[Et_4N][W(CCMe_3)Cl_4]}$ (2.1 g, 4.0 mmol) in 10 mL of tetrahydrofuran. The solution immediately became homogeneous blue-green. After 3 h the THF solution was cooled to −30 °C. Ether- or pentane-insoluble light blue crystals (1.1 g) were isolated by filtration. The filtrate was concentrated in vacuo and cooled to −30 °C for a second crop (0.5 g): ^{1}H NMR ($\mathrm{CDCl_3}$) δ 3.36 (q, 8, J_{HH} = 6.1 Hz, $\mathrm{NC}H_2\mathrm{CH_3}$), 2.15 (m, 6, $\mathrm{PC}H_2\mathrm{CH_3}$), 1.29 (br t, 12, $\mathrm{NCH_2C}H_3$), 1.23 (s, 9, $\mathrm{CCMe_3}$), 1.14 (m, 9, $\mathrm{PCH_2C}H_3$); ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$) δ 335.0 (d, $^2J_{CP}$ = 13.2 Hz, $C\mathrm{CMe_3}$), 52.0 ($\mathrm{N}C\mathrm{H_2CH_3}$), 45.4 ($\mathrm{C}C\mathrm{Me_3}$), 34.3 ($\mathrm{CC}Me_3$), 18.4 (d, J_{CP} = 26 Hz, $\mathrm{P}C\mathrm{H_2CH_3}$), 7.28 (br s, $\mathrm{NCH_2}C\mathrm{H_3}$ and $\mathrm{PCH_2}C\mathrm{H_3}$); ^{31}P{^{1}H} NMR ($\mathrm{CDCl_3}$) δ 34.3 (J_{PW} = 259 Hz). Anal. Calcd for $\mathrm{WC_{19}H_{44}NPCl_4}$: C, 35.48; H, 6.90. Found: C, 34.86; H, 6.66.

$\mathbf{W(CCMe_3)(dme)Cl_3}$. A pentane solution (60 mL) containing $\mathrm{W(CCMe_3)Np_3}$ (10.0 g, 21.4 mmol) and dimethoxyethane (5.8 g, 64.4 mmol) was cooled in an ice bath, and a 3.3 M solution of HCl in ether (25 mL, 83 mmol) was added dropwise (5 min). A blue-purple precipitate formed near the end of the addition. The reaction was stirred for 0.5 h, and the solid was filtered off, washed with pentane, and dried in vacuo (7.92 g). Cooling the filtrate (containing the pentane washings) to −30 °C gave a second crop of purple crystals (0.86 g) for a total yield of 8.78 g (91%): ^{1}H NMR (toluene-d_8) δ 3.66 and 3.27 (s, 6, $Me\mathrm{OCH_2CH_2O}Me$), 3.02 and 2.92 (m, 4, $\mathrm{MeOC}H_2\mathrm{C}H_2\mathrm{OMe}$), 1.26 (s, 9, $\mathrm{CCMe_3}$); ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$) δ 335.1 (s, J_{CW} = 224 Hz, $C\mathrm{CMe_3}$), 78.4 (t, J_{CH} = 151 Hz, $\mathrm{MeO}C\mathrm{H_2CH_2OMe}$), 76.3 (q, J_{CH} = 149 Hz, $Me\mathrm{OCH_2CH_2OMe}$), 69.6 (t, J_{CH} = 146 Hz, $\mathrm{MeOCH_2}C\mathrm{H_2OMe}$), 59.3 (q, J_{CH} = 146 Hz, $\mathrm{MeOCH_2CH_2O}Me$), 47.7 (s, $\mathrm{C}C\mathrm{Me_3}$), 33.7 (q, J_{CH} = 128 Hz, $\mathrm{CC}Me_3$). Anal. Calcd for $\mathrm{WC_9H_{19}Cl_3O_2}$: C, 24.05; H, 4.26. Found: C, 24.26; H, 4.25.

$\mathbf{W(CCMe_3)(Et_3PO)Cl_3}$. (i) From $\mathbf{W(O)(CHCMe_3)(PEt_3)_2Cl_2}$. The color of a solution of $\mathrm{W(O)(CHCMe_3)(PEt_3)_2Cl_2}$ (1.0 g, 1.73 mmol) and $\mathrm{C_2Cl_6}$ (0.41 g, 1.73 mmol) in 5 mL of THF changed from yellow to blue over a period of 10 h. White, crystalline $\mathrm{[PEt_3H][Cl]}$ (0.21 g, 78%) was collected by filtration. Pentane (2 mL) was added, and additional $\mathrm{[PEt_3H][Cl]}$ was filtered off. The solvent was removed in vacuo from the filtrate to yield a royal blue oil (0.83 g, 98%): ^{1}H NMR ($\mathrm{CDCl_3}$) δ 2.16 (br m, 6, $\mathrm{PC}H_2\mathrm{CH_3}$), 1.31 (br m, 9, $\mathrm{PCH_2C}H_3$), 1.22 (s, 9, $\mathrm{CCMe_3}$); ^{13}C NMR ($\mathrm{C_6D_6}$) δ 329 (s, J_{CW} = 208 Hz, $C\mathrm{CMe_3}$), 46.1 (s, $\mathrm{C}C\mathrm{Me_3}$), 34.9 (q, J_{CH} = 127 Hz, $\mathrm{CC}Me_3$), 17.9 (dt, J_{CH} = 124 Hz, J_{CP} = 63 Hz, $\mathrm{P}C\mathrm{H_2CH_3}$), 5.64 (q, J_{CH} = 124 Hz, $\mathrm{PCH_2}C\mathrm{H_3}$); ^{31}P{^{1}H} NMR ($\mathrm{CDCl_3}$) δ 82.4.

(ii) From $\mathbf{W(O)(CHCMe_3)(PEt_3)Cl_2}$. $\mathrm{W(O)(CHCMe_3)(PEt_3)Cl_2}$ (0.2 g, 0.44 mmol) and $\mathrm{PEt_3Cl_2}$ (0.08 g, 0.44 mmol) were stirred in 3 mL of $\mathrm{CH_2Cl_2}$ for 2 h. The color of the yellow reaction mixture turned blue and white crystals of $\mathrm{[PEt_3H][Cl]}$ formed in the solution. The reaction mixture was filtered and the solvent removed in vacuo to yield a blue oil which was identical with that above by ^{1}H and ^{13}C NMR spectroscopy.

$\mathbf{W(CCMe_3)(Et_3PO)(PEt_3)Cl_3}$. $\mathrm{W(O)(CHCMe_3)(PEt_3)_2Cl_2}$ (1.0 g, 1.73 mmol) and $\mathrm{C_2Cl_6}$ (0.41 g, 1.73 mmol) were dissolved in a mixture of 5 mL of THF and 3 mL of ether. After 12 h the reaction mixture was blue, and 0.25 g (93%) of $\mathrm{[PEt_3H]Cl}$ had precipitated. The reaction mixture was filtered, and $\mathrm{PEt_3}$ (0.20 g, 1.73 mmol) was added to the filtrate. The resulting green solution was filtered, and the solvent was removed in vacuo to give a green oil. The oil was dissolved in a minimum amount of ether, and pentane was added until crystallization began. A total of 0.95 g of turquoise blue $\mathrm{W(CCMe_3)(Et_3PO)(PEt_3)Cl_3}$ (90%) was obtained in two crops: ^{1}H NMR ($\mathrm{C_6D_6}$) δ 1.82 (dq, 6, $^3J_{HH}$ = 7.7 Hz, $^2J_{HP}$ = 8.3 Hz, $\mathrm{OPC}H_2\mathrm{CH_3}$), 1.61 (dq, 6, $^3J_{HH}$ = 7.4 Hz, $^2J_{HP}$ = 6.3 Hz, $\mathrm{PC}H_2\mathrm{CH_3}$), 1.37 (s, 9, $\mathrm{CCMe_3}$), 1.00 (dt, 9, $^3J_{HH}$ = 7.4 Hz, $^3J_{HP}$ = 15 Hz, $\mathrm{PCH_2C}H_3$), 0.88 (dt, 9, $^3J_{HH}$ = 7.7 Hz, $^3J_{HP}$ = 17 Hz, $\mathrm{OPCH_2C}H_3$); ^{13}C NMR ($\mathrm{C_6D_6}$) δ 340 (d, $^2J_{CP}$ = 14.5 Hz, $C\mathrm{CMe_3}$), 46.9 (s, $\mathrm{C}C\mathrm{Me_3}$), 35.1 (q, J_{CH} = 128 Hz, $\mathrm{CC}Me_3$), 19.1 (dt, J_{CH} = 128 Hz, J_{CP} = 58 Hz, $\mathrm{OP}C\mathrm{H_2CH_3}$), 18.5 (dt, J_{CH} = 131

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Hz, J_{CP} = 23 Hz, P*C*H$_2$CH$_3$), 7.2 (q, J_{CH} = 128 Hz, PCH$_2$*C*H$_3$), 5.9 (q, J_{CH} = 125 Hz, OPCH$_2$*C*H$_3$); the minor isomer shows a signal for C$_\alpha$ at 338 ppm ($^2J_{CP}$ = 14.5 Hz), major isomer/minor isomer $\simeq$ 10; ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 63.9 (Et$_3$PO), 33.2 (J_{PW} = 256 Hz, PEt$_3$); IR (Nujol) 1117 cm^{-1} (νP=O). Anal. Calcd for WC$_{17}$H$_{39}$Cl$_3$P$_2$O: C, 33.38; H, 6.43. Found: C, 33.70; H, 6.46.

W(CCMe$_3$)(PMe$_3$)$_3$Cl$_3$. W(O)(CHCMe$_3$)(PEt$_3$)$_2$Cl$_2$ (2.0 g, 3.46 mmol) and C$_2$Cl$_6$ (0.82 g, 3.46 mmol) were dissolved in a mixture of 5 mL of THF and 3 mL of ether. After 12 h 0.51 g (94%) of [PEt$_3$H][Cl] was removed from the blue solution by filtration. PMe$_3$ (1.1 mL, 11.6 mmol) was added by syringe to the blue filtrate. After 10 min yellow, crystalline W(CCMe$_3$)(PMe$_3$)$_3$Cl$_3$ (2.0 g, 98%) was collected by filtration: ^{1}H NMR (CDCl$_3$) δ 1.66 (t, 27, $^2J_{HP}$ = 9.8 Hz, PMe$_3$), 1.42 (s, 9, CCMe$_3$); ^{13}C NMR (CDCl$_3$) δ 401 (q, $^2J_{CP}$ = 40 Hz, *C*CMe$_3$), 56.7 (s, C*C*Me$_3$), 34.4 (q, J_{CH} = 125 Hz, CC*Me*$_3$), 18.7 (qq, J_{CH} = 137 Hz, J_{CP} = 11.6 Hz, PMe$_3$); ^{31}P{^{1}H} NMR (CDCl$_3$) δ 19.4 (J_{PW} = 247 Hz); conductivity 7.4 cm^{-1} Ω^{-1} M^{-1} in CH$_2$Cl$_2$. Anal. Calcd for WC$_{14}$H$_{36}$Cl$_3$P: C, 28.62; H, 6.18. Found: C, 29.08; H, 6.25.

After W(CCMe$_3$)(PMe$_3$)$_3$Cl$_3$ was filtered off, the volatiles were removed from the filtrate in vacuo to give a quantitative yield of Et$_3$PO which was identical by NMR and IR with an authentic sample.

Preparation of W(CCMe$_3$)(PMe$_3$)$_3$Cl$_3$ from W(O)(CHCMe$_3$)(PEt$_3$)Cl$_2$ Using PPr$_3$Cl$_2$. W(O)(CHCMe$_3$)(PEt$_3$)Cl$_2$ (0.35 g, 0.76 mmol) and PPr$_3$Cl$_2$ (0.18 g, 0.76 mmol) were dissolved in 2 mL of THF. The solution turned blue almost immediately. After 1 day 0.10 g of [PEt$_3$H][Cl] (93%) was removed by filtration and PMe$_3$ (0.25 mL, 2.63 mmol) added by syringe to the blue filtrate. After 10 min, 0.40 g (89%) of W(CCMe$_3$)(PMe$_3$)$_3$Cl$_3$ was collected by filtration. The solvent was removed in vacuo from the filtrate, giving 0.11 g (85%) Pr$_3$PO which was identical with an authentic sample.

W(CCMe$_3$)(PMe$_3$)$_2$Cl$_3$. Hexachloroethane (0.28 g, 1.19 mmol) was added to a stirred solution of W(CCMe$_3$)(PMe$_3$)$_3$Cl$_3$ (0.70 g, 1.19 mmol) in 5 mL of CH$_2$Cl$_2$. [PMe$_3$Cl][Cl] precipitated immediately. After 1 h the mixture was filtered and the solvent removed from the filtrate in vacuo to yield a yellow oil. The oil was extracted with 10 mL of ether, and the resulting solution was filtered to remove additional [PMe$_3$Cl][Cl]. Addition of pentane and cooling produced 0.52 g (85%) of yellow crystals: ^{1}H NMR (CDCl$_3$) δ 1.79 (d, 18, $^2J_{HP}$ = 9.8 Hz, PMe$_3$), 1.25 (s, 9, CCMe$_3$); ^{13}C NMR (CDCl$_3$) δ 357 (t, $^2J_{CP}$ = 2 Hz, *C*CMe$_3$), 54.1 (s, C*C*Me$_3$), 32.8 (q, J_{CH} = 125 Hz, CC*Me*$_3$), 16.4 (dq, J_{CH} = 131 Hz, J_{CP} = 37 Hz, PMe$_3$); ^{31}P{^{1}H} NMR (CDCl$_3$) δ 26.1 (J_{PW} = 173 Hz). Anal. Calcd for WC$_{11}$H$_{27}$Cl$_3$P$_2$: C, 25.83; H, 5.32. Found: C, 26.21; H, 5.39.

W(CCMe$_3$)(PMe$_3$)Cl$_3$. Hexachloroethane (0.66 g, 2.79 mmol) was added to a stirred solution of W(CCMe$_3$)(PMe$_3$)$_3$Cl$_3$ (0.82 g, 1.40 mmol) dissolved in 5 mL of CH$_2$Cl$_2$. The reaction mixture turned violet as [PMe$_3$Cl][Cl] precipitated from solution. After 2 h the mixture was filtered and the solvent was removed from the filtrate in vacuo. The violet solid was washed with ether and recrystallized from toluene by addition of pentane (0.51 g, 84%): ^{1}H NMR (CDCl$_3$) δ 1.71 (d, 9, $^2J_{HP}$ = 10.4 Hz, PMe$_3$), 1.64 (s, 9, CCMe$_3$); ^{13}C NMR (CDCl$_3$) δ 345 (d, $^2J_{CP}$ = 12 Hz, *C*CMe$_3$), 50.0 (s, C*C*Me$_3$), 33.1 (q, J_{CH} = 125 Hz, CC*Me*$_3$), 17.7 (dq, J_{CH} = 131 Hz, J_{CP} = 34 Hz, PMe$_3$); ^{31}P{^{1}H} NMR (CDCl$_3$) δ 16.0 (J_{PW} = 259 Hz). Anal. Calcd for WC$_8$H$_{18}$Cl$_3$P: C, 22.07; H, 4.17. Found: C, 22.29; H, 4.30.

W(CCMe$_3$)(PEt$_3$)Cl$_3$. (i) From W(CCMe$_3$)(Et$_3$PO)(PEt$_3$)Cl$_3$. W(CCMe$_3$)(Et$_3$PO)(PEt$_3$)Cl$_3$ (1.08 g, 1.77 mmol) was dissolved in 5 mL of dichloromethane and freshly sublimed AlCl$_3$ (0.24 g, 1.77 mmol) was added. After 10 min all of the AlCl$_3$ had dissolved and the solution was violet. The solvent was removed in vacuo, and the residue was dissolved in a minimal amount of toluene (~5 mL). Pentane was slowly added until a yellow oil formed on the walls of the reaction vessel. The purple solution was decanted away, and more pentane was added to it to give 0.79 g (94%) of crystalline W(CCMe$_3$)(PEt$_3$)Cl$_3$ after the solution was let stand for several hours at −30 °C: ^{1}H NMR (C$_6$D$_6$) δ 1.56 (dq, 6, $^3J_{HH}$ = 7.3 Hz, $^2J_{HP}$ = 7.9 Hz, PC*H*$_2$CH$_3$), 1.20 (s, 9, CCMe$_3$), 0.76 (dt, 9, $^3J_{HH}$ = 7.3 Hz, $^3J_{HP}$ = 16.5 Hz, PCH$_2$C*H*$_3$); ^{13}C NMR (C$_6$D$_6$) δ 346 (d, $^2J_{CP}$ = 13 Hz, J_{CW} = 209 Hz, *C*CMe$_3$), 50.9 (s, C*C*Me$_3$), 32.9 (q, J_{CH} = 125 Hz, CC*Me*$_3$), 18.8 (dt, J_{CH} = 129 Hz, J_{CP} = 29 Hz, P*C*H$_2$CH$_3$), 8.2 (q, J_{CH} = 129 Hz, PCH$_2$*C*H$_3$); ^{31}P{^{1}H} NMR δ 43.5 (J_{PW} = 237 Hz). Anal. Calcd for WC$_{11}$H$_{24}$Cl$_3$P$_4$: C, 27.67; H, 5.07. Found: C, 27.98; H, 5.07.

(ii) From [NEt$_4$][W(CCMe$_3$)Cl$_4$]. ZnCl$_2$(PEt$_3$) (1.02 g, 4.0 mmol; prepared from ZnCl$_2$(dioxane) and PEt$_3$) was added with stirring to [NEt$_4$][W(CCMe$_3$)Cl$_4$] (2.08 g, 4.0 mmol) in dichloromethane (10 mL). The blue solution immediately turned violet. The mixture was filtered through Celite, and the filtrate was evaporated in vacuo to yield violet microcrystals (1.72 g, 90%).

W(CCMe$_3$)(OCMe$_3$)$_3$. A solution of LiOCMe$_3$ (0.96 g, 12 mmol) in 20 mL of ether was rapidly added to a solution of [NEt$_4$][W(CCMe$_3$)Cl$_4$] (2.1 g, 4 mmol) in 40 mL of THF which had been cooled to −30 °C. After 3 h the mixture was filtered through Celite, and the solvent was removed from the filtrate in vacuo. The resulting brown solid was extracted with pentane and the mixture was filtered. The pentane was removed from the filtrate in vacuo, and the residue was sublimed at 50 °C and 1 μm to give light yellow crystalline W(CCMe$_3$)(OCMe$_3$)$_3$ (85%). The yellow coloration is due to trace impurities since colorless crystals can be obtained by adding acetonitrile to a concentrated solution of W(CCMe$_3$)(OCMe$_3$)$_3$ in ether and cooling it to −30 °C: ^{1}H NMR (CDCl$_3$) δ 1.23 (s, 9, CCMe$_3$), 1.43 (s, 27, OCMe$_3$); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 271 (*C*CMe$_3$), 78.6 (O*C*Me$_3$), 49.5 (C*C*Me$_3$), 33.9 (CC*Me*$_3$), 32.3 (OC*Me*$_3$); M_r (CH$_2$Cl$_2$, differential vapor pressure, 0 °C) calcd 472, found 437 at 0.082 M. Anal. Calcd for WC$_{17}$H$_{36}$O$_3$: C, 43.23; H, 7.68. Found: C, 43.06; H, 7.69.

W(CCMe$_3$)(NMe$_2$)$_3$. A solution of LiNMe$_2$ (0.31 g, 6.0 mmol) in THF (10 mL) was added to a solution of [NEt$_4$][W(CCMe$_3$)Cl$_4$] (1.05 g, 2 mmol) in THF (25 mL) which had been cooled to −30 °C. The reaction was allowed to warm to room temperature. The yellow-red reaction mixture was filtered, and the solvent was removed from the filtrate in vacuo. The residue was extracted with pentane, the mixture was filtered, and the pentane was removed from the filtrate in vacuo. The resulting red solid was sublimed at 70 °C and 1 μm to give 0.35 g of pale yellow W(CCMe$_3$)(NMe$_2$)$_3$: ^{1}H NMR (C$_6$D$_6$) δ 1.36 (CMe$_3$), 3.34 (NMe$_2$); ^{13}C NMR (C$_6$D$_6$) δ 288.3 (*C*CMe$_3$), 51.85 (C*C*Me$_3$), 50.58 (NMe$_2$), 32.74 (CC*Me*$_3$). Anal. Calcd for WC$_{11}$H$_{27}$N$_3$: C, 34.30; H, 7.07. Found: C, 34.08; H, 6.88.

W(CCMe$_3$)(N-*i*-Pr$_2$)$_3$. A reaction similar to the one above employing 2.1 g (4 mmol) of [NEt$_4$][W(CCMe$_3$)Cl$_4$] in 40 mL of THF and 1.28 g (12 mmol) of LiN-*i*-Pr$_2$ in 15 mL of THF gave a 50% yield of yellow W(CCMe$_3$)(N-*i*-Pr$_2$)$_3$ by sublimation at 70 °C and 1 μm: ^{1}H NMR (CDCl$_3$) δ 1.09 (d, 18, J_{HH} = 6 Hz, NCH*Me*Me′), 1.27 (d, 18, J_{HH} = 6 Hz, NCHMe*Me′*), 1.41 (s, 9, CC*Me*$_3$), 3.7 (m, 6, NC*H*Me$_2$).

W(CCMe$_3$)(SCMe$_3$)$_3$. A procedure similar to that used to prepare W(CCMe$_3$)(NMe$_2$)$_3$ employing 1.05 g (2 mmol) of [NEt$_4$][W(CCMe$_3$)Cl$_4$] in 30 mL of THF and 0.57 g (6 mmol) of LiSCMe$_3$ in THF gave 0.5 g of orange W(CCMe$_3$)(SCMe$_3$)$_3$ by sublimation: ^{1}H NMR (CDCl$_3$) δ 1.59 (s, 27, SCMe$_3$), 1.41 (s, 9, CCMe$_3$); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 334.5 (*C*CMe$_3$), 55.7 (C*C*Me$_3$), 49.51 (S*C*Me$_3$), 36.25 (SC*Me*$_3$), 31.76 (CC*Me*$_3$). Anal. Calcd for WC$_{17}$H$_{36}$S$_3$: C, 39.23; H, 6.97. Found: C, 39.12; H, 7.05.

[W(CCMe$_3$)(OMe)$_3$(HNMe$_2$)]$_2$. A toluene solution (8 mL) of methanol (116 μL, 2.9 mmol) was cooled to −30 °C, and a solution of W(CCMe$_3$)(NMe$_2$)$_3$ (0.37 g, 0.96 mmol) in toluene (2 mL) was added dropwise. After 2 h at room temperature the volatiles were removed in vacuo, leaving yellow crystals which were recrystallized from ether at −30 °C (0.34 g, 90%): ^{1}H NMR (C$_6$D$_6$) δ 5.26, 5.04, 4.68 (s, 9, OMe), 2.94 (d, 3, $^3J_{H_AH}$ = 5.9 Hz, HN*Me*$_A$Me$_B$), 2.45 (d, 3, $^3J_{H_BH}$ = 5.9 Hz, HNMe$_A$*Me*$_B$), 1.15 (s, 9, CCMe$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 286.0 (s, *C*CMe$_3$), 72.1 (q, J_{CH} = 139 Hz, OMe), 71.1 (q, J_{CH} = 139 Hz, OMe), 67.0 (q, J_{CH} = 140 Hz, OMe), 48.7 (qd, J_{CH} = 139 Hz, $^2J_{C_AH} \approx$ 6 Hz, HN*Me*$_A$Me$_B$), 48.5 (s, C*C*Me$_3$), 42.7 (qd, $J_{CH} \approx$ 137 Hz, $^2J_{C_BH} \approx$ 6 Hz, HNMe$_A$*Me*$_B$), 35.7 (q, J_{CH} = 130 Hz, CC*Me*$_3$); M_r (CH$_2$Cl$_2$, differential vapor pressure, 0 °C) calcd 782, found 837 at 4.4×10^{-2} M. Anal. Calcd for WC$_{10}$H$_{25}$NO$_3$: C, 30.71; H, 6.44. Found: C, 30.99; H, 6.32.

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Registry No. $W(CCMe_3)NP_3$, 68490-69-7; $W(CCMe_3)(OCMe_3)_3$, 78234-36-3; $W(CCMe_3)(NMe_2)_3$, 82209-29-8; $W(CCMe_3)(SCMe_3)_3$, 83416-64-2; $[W(CCMe_3)(OMe)_3(NMe_2H)]_2$, 83416-65-3; $[PEt_3H][W(CCMe_3)Cl_4]$, 83416-67-5; $[NEt_4][W(CCMe_3)Cl_4]$, 78251-20-4; $[NEt_4][W(CCMe_3(PEt_3)Cl_4]$, 83416-69-7; $W(CCMe_3)(dme)Cl_3$, 83416-70-0; $W(CCMe_3)(Et_3PO)Cl_3$, 78251-21-5; $W(CCMe_3)(Et_3PO)(PEt_3)Cl_3$, 78481-48-8; $W(CCMe_3)(PMe_3)_3Cl_3$, 78251-18-0; $W(CCMe_3)(PMe_3)_2Cl_3$, 83461-72-7; $W(CCMe_3)(PMe_3)Cl_3$, 83416-71-1; $W(CCMe_3)(PEt_3)Cl_3$, 82661-16-3; $W(CCMe_3)(N\text{-}i\text{-}Pr_2)_3$, 82810-47-7.

A Useful Dienemethylation Agent: 2,4-Pentadienyltrimethylsilane[†]

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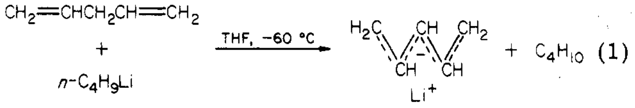
(*E*)- or (*Z*)-2,4-pentadienyltrimethylsilane reacts with aldehydes and ketones in dichloromethane solution in the presence of $TiCl_4$ to give, after hydrolysis, alcohols of type $RCH(OH)CH_2CH{=}CHCH{=}CH_2$ and $RR'C(OH)CH_2CH{=}CHCH{=}CH_2$, respectively (*E* isomer only), in generally good yield. Experiments with (*Z,E*)-2,4-hexadienyltrimethylsilane showed that an S_E2' process is operative, since with aldehydes the products were of the type $RCH(OH)CH(CH_3)CH{=}CHCH{=}CH_2$. $Me_3SiCH_2CH{=}CHCH{=}CH_2$ also reacted with acetals and ketals to replace an alkoxy group with $CH_2CH{=}CHCH{=}CH_2$.

Introduction

In principle, pentadienyllithium, 1, whose preparation and structure in solution was reported by Bates and his co-workers in 1967 (eq 1),[2] should be a useful reagent for the introduction of the $CH_2{=}CHCH{=}CHCH_2$ group into diverse organic structures by standard organolithium methodology. In practise, this is not the case since pentadienyllithium reacts with aldehydes[3] and ketones[4] to give, after hydrolysis, a mixture of isomeric alcohols, as shown in eq 2 and 3, in which the new C–C bonds have been formed at the central as well as at the terminal carbon atoms of the reagent. The addition of 1 to the C=O bond of aliphatic aldehydes was found to be irreversible, but reversibility could be demonstrated in the case of the reaction of 1 with ketones. Thus, when the THF solution of the lithium alkoxide mixture formed in some (but not all) of the 1/ketone reactions was heated at 60 °C for 5 h, the isomer mixture was converted to a single isomer, the dienylmethyl alkoxide $CH_2{=}CHCH{=}CHCH_2CR_2OLi$.[4] For instance, such was found to be the case in the 3-pentanone reaction.



1

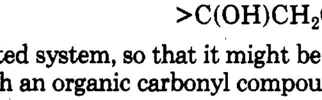
$$\mathrm{Li(CH_2CHCHCHCH_2) + C_2H_5CH{=}O \xrightarrow{THF,\ 20\ ^\circ C} \xrightarrow{H_2O} \underset{31\ parts}{(CH_2{=}CH)_2CHCH(OH)C_2H_5} + \underset{69\ parts}{CH_2{=}CHCH{=}CHCH_2CH(OH)C_2H_5}} \quad (2)$$

$$\mathrm{Li(CH_2CHCHCHCH_2) + (C_2H_5)_2C{=}O \xrightarrow{THF,\ 20\ ^\circ C} \xrightarrow{H_2O} \underset{44\ parts}{(CH_2{=}CH)_2CHC(OH)(C_2H_5)_2} + \underset{56\ parts}{CH_2{=}CHCH{=}CHCH_2C(OH)(C_2H_5)_2}} \quad (3)$$

It seemed to us that a reagent which could add the pentadienyl group to the C=O bond of aldehydes and ketones under mild conditions to give exclusively products of type $RR'C(OH)CH_2CH{=}CHCH{=}CH_2$ would be a useful addition to the arsenal of the synthetic organic chemist. We have found such a reagent in 2,4-pentadienyltrimethylsilane, $(CH_3)_3SiCH_2CH{=}CHCH{=}CH_2$.

Results and Discussion

In contrast to the C=O additions of pentadienyllithium, the reaction of this reagent with trimethylchlorosilane was regiospecific, giving only (*E*)-2,4-pentadienyltrimethylsilane, 2, in high yield. This compound is, in a sense, an allylic silane, and as such it possibly could react with aldehydes and ketones in the presence of a Lewis acid (as do allylsilanes: eq 4[5]). In the case of 2, we are dealing with a conjugated system, so that it might be expected that its reaction with an organic carbonyl compound would take the course shown in eq 5.



2

$$\mathrm{R_3SiCH_2CH{=}\overset{*}{C}H_2 + {>}C{=}O \xrightarrow{Lewis\ acid} \xrightarrow{hydrolysis} {>}C(OH)\overset{*}{C}H_2CH{=}CH_2} \quad (4)$$

$$\mathrm{(CH_3)_3SiCH_2CH{=}CHCH{=}\overset{*}{C}H_2 + {>}C{=}O \xrightarrow{Lewis\ acid} \xrightarrow{hydrolysis} {>}C(OH)\overset{*}{C}H_2CH{=}CHCH{=}CH_2} \quad (5)$$

[†] Dedicated to the memory of Rolly Pettit, a friend and a brilliant and imaginative chemist.

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