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A CONVENIENT SYNTHESIS OF TRIALKYLALKYLIDYNE TUNGSTEN (6+) COMPOUNDS AND THE X-RAY CRYSTAL STRUCTURE OF $(Me_3CCH_2)_3W{\equiv}CPh(py)$

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Abstract—A convenient synthesis for trialkylalkylidyne tungsten compounds is reported based on the metathetic reaction between alkyllithium or alkyl-Grignard reagents and $(^tBuO)_3W{\equiv}CR$ compounds. The success of the strategy is limited to alkyl ligands that lack β-hydrogen atoms. The X-ray crystal structure of $(Me_3CCH_2)_3W{\equiv}CPh(py)$ is reported. Cell dimensions at $-155°C$: $a = 13.657(7)$, $b = 13.897(9)$, $c = 14.115(7)$ Å, $Z = 4$ and space group $P2_12_12_1$. The central WC_4N unit is based on a distorted trigonal bipyramid with axial alkylidyne and pyridine ligands, with W—C = 1.74(3) and W—N = 2.57(3) Å, respectively.

As part of our long-standing interest in Group VI organometallic and inorganic chemistry we have become interested in exploring new, molecular routes to carbides, nitrides and oxides of molybdenum and tungsten.[1] We believe that trialkyltungstenalkylidynes, R'_3WCR, will serve as low temperature precursors to tungsten carbides (WC or W_2C). Girolami and his co-workers[2] have reported the formation of titanium carbide in the decomposition of $Ti(CH_2CMe_3)_4$ at temperatures as low as 150°C.

As we begin this work there are only a few examples of tungsten alkylidynes supported exclusively by alkyl ligands. These are prepared by reactions involving multiple α-hydrogen abstractions and are specific for Me_3SiCH_2 and Me_3CCH_2 ligands.[2] We require a more general method and chose to investigate metathetic reactions involving $(^tBuO)_3WCR$ complexes.

RESULTS AND DISCUSSION

Synthesis

Reaction of the alkoxide supported alkylidyne $(^tBuO)_3WCR$ with alkyl-Grignard or alkyl-lithium reagents of the type RCH_2M results in the formation of the desired trialkylalylidynes as shown in eq. (1). As the complexes $(^tBuO)_3WCR$ can be made with a wide variety of different R groups by the reaction of $W_2(O^tBu)_6$ with RCCR,[3] this route has the potential to be quite general. Table 1 lists the compounds made by this route so far, along with selected ^{13}C NMR data for their alkylidyne ligands. All of the new compounds have been characterized by ^1H and ^{13}C NMR spectroscopies, elemental analysis in most cases, and for $(Me_3CCH_2)_3WCPh(py)$ by single crystal X-ray crystallography.

Table 1. New alkylalkylidyne tungsten compounds with selected ^{13}C NMR data for the alkylidyne carbon

	Chemical shift (ppm)	J_{WC} (Hz)
$(PhCH_2)_3WC^tBu$	297.5	n.o.
$(Me_3CCH_2)_3WCSiMe_3$	338.3	188.7
$(Me_3SiCH_2)_3WCPh$	303.6	221.0
$((Me_3SiCH_2)_3WC)_2$	314.4	n.o.
$(Me_3CCH_2)_3WCPh \cdot py$	283.4	n.o.
$(Me_3SiCH_2)_3WCPh \cdot py$	n.o.	—
$((Me_3CCH_2)_3WC)_2$	n.o.	—
$(py(Me_3CCH_2)_3WC)_2$	305.3	n.o.
$(Me_3SiCH_2)_3WC^tBu$	319.5	215.0

n.o. = not observed.

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$$({}^tBuO)_3W{\equiv}CR + 3\,LiR' \longrightarrow (R')_3W{\equiv}CR + 3\,{}^tBuOLi. \quad (1)$$

Compounds containing benzyl or neopentyl ligands have only been prepared using the Grignard or lithium reagents, respectively. This is simply due to the convenience of these reagents relative to benzyllithium or neopentyl-Grignard. Compounds with Me_3SiCH_2 ligands can be made equally well from Me_3SiCH_2MgCl or Me_3SiCH_2Li. In some cases, when alkyl-lithium reagents were used it was difficult to separate the ${}^tBuOLi$ formed from the desired product. A useful procedure in this situation was to add a stoichiometric amount of $BF_3 \cdot OEt_2$ to a cooled hexane solution of the mixture. This quantitatively precipitated $BF_3({}^tBuO)Li$ which was then removed by filtration.

As expected, the stability and physical properties of the trialkylalkylidynes depended markedly on the substituents R and R′. Although combinations of large R and R′ groups give the best stability, steric and electronic factors cannot be separated at this point. The importance of the alkylidyne substituent, R, in determining the stability of these complexes is underscored by the relative stabilities of $(PhCH_2)_3WCR$ (R = ${}^tBu$, Me_3Si, Ph). The neopentylidyne is a yellow crystalline solid which is indefinitely stable in the absence of air or moisture. The trimethylsilylmethylidyne can be detected in solution (${}^1H$ NMR: $PhCH_2$ 2.18 ppm, J_{WH} = 7.7 Hz) but decomposes at a rate similar to that of its formation from $({}^tBuO)_3WCSiMe_3$ and $PhCH_2MgCl$ and cannot be isolated. The benzylidyne has never been detected. Likewise, no evidence for a complex with an ethylidyne ligand $(RCH_2)_3WCMe$ has ever been seen with any alkyl ligand.

Of the alkyl ligands investigated, Me_3CCH_2 and Me_3SiCH_2 most effectively stabilize the alkylalkylidynes. In these series even compounds with relatively small alkylidyne substituents such as phenyl, and the dimers $(RCH_2)_3WC\text{-}CW(CH_2R)_3$, can be made and are relatively stable. The mixed neopentyl/trimethylsilylmethyl complexes $(Me_3CCH_2)_3WCSiMe_3$ and $(Me_3SiCH_2)_3WCCMe_3$ are both quite volatile, the latter subliming with little or no decomposition at *ca* 10^{-3} Torr and 50–55°C. The former compound is an oil and although small amounts of it can be distilled onto a cold finger condenser, attempted distillation on larger scales causes extensive decomposition. The benzylidynes, $(Me_3SiCH_2)_3WCPh$ and $(Me_3CCH_2)_3WCPh$, are oils at room temperature and decompose upon attempted distillation. Their pyridine adducts are, however, crystalline allowing purification of these compounds. The X-ray crystal structure of one of these is presented below.

We have not had as much success with other alkyl ligands. Only one complex containing benzyl ligands has been isolated, and with smaller alkyl groups or those with β-hydrogens (Me_2CHCH_2, Me_2CH) we have found no evidence for formation of R'_3WCR complexes.

NMR studies

The ${}^1H$ and ${}^{13}C$ NMR spectra are consistent with the formulation of these complexes as being monomeric with C_3 symmetry. The ${}^{13}C$ NMR spectra show characteristic far downfield chemical shifts and large values of J_{WC} for the alkylidyne carbon atoms (see Table 1). The alkylidyne chemical shifts range from 283.8 to 327.0 ppm; in each case this is about 30 ppm downfield of the corresponding $({}^tBuO)_3WCR$ complex. Tungsten coupling of 75–90 Hz is also observed to the carbon atoms of the methylene groups. In the ${}^1H$ NMR spectra, small ${}^{183}W\text{–}{}^1H$ couplings (6–11 Hz) are seen to the hydrogen atoms of the methylene groups.

Molecular structure of $(Me_3CCH_2)_3W{\equiv}CPh(py)$

A summary of crystal data is given in Table 2 and selected bond distances and bond angles are given in Table 3. A ball-and-stick drawing of the molecule is shown in Fig. 1.

The central WC_4N core is a distorted trigonal pyramid in which the alkylidyne carbon and pyridine nitrogen occupy *trans* positions: N(15)—W—C(21) = 179.5(10)°. The W—C triple bond distance, 1.74(3) Å, and the W—C (neopentyl) distances, 2.13(4) Å, are well within the range expected based on other alkylalkylidyne compounds of tungsten (6+). The W—N (pyridine) distance of 2.575(25) Å is very long, indicative of a relatively weak donor interaction. The alkylidyne—C—W—C (alkyl) angles of *ca* 100° are similar to those seen in related trigonal bipyramidal structures such as $[({}^tBuO)_3W{\equiv}N]_\infty$[3] and $({}^tBuO)_3W(NO)(py)$[4] where the equatorial ligands bend away from the multiple bond in one axial site and toward the weak donor ligand in the other axial position.

Concluding remarks

The reported procedure provides a convenient synthesis for a number of trialkylalkylidyne tungsten compounds. Studies of their modes of thermal decomposition are currently underway.

Table 2. Summary of crystal data for $(Me_3CCH_2)_3W{\equiv}CPh(py)$

Empirical formula	$WC_{27}H_{43}N$
Colour of crystal	Reddish green?
Crystal dimensions (mm)	0.25 × 0.25 × 0.25
Space group	$P2_12_12_1$
Cell dimensions	
Temperature (°C)	−155
a (Å)	13.657(7)
b (Å)	13.897(9)
c (Å)	14.115(7)
Z (molecules/cell)	4
Volume (Å^3)	2679.03
Calculated density (g cm^{-3})	1.402
Wavelength (Å)	0.71069
Molecular weight	565.49
Linear absorption coefficient (cm^{-1})	44.148
Detector to sample distance (cm)	22.5
Sample to source distance (cm)	23.5
Average omega scan width at half height	0.25
Scan speed (deg min^{-1})	4.0
Scan width (deg + dispersion)	1.8
Individual background (s)	8
Aperture size (mm)	3.0 × 4.0
2θ Range (deg)	6–45
Total number of reflections collected	2744
Number of unique intensities	2000
Number with $F > 0.0$	1896
Number with $F > 2.33\sigma(F)$	1754
$R(F)$	0.0649
$Rw(F)$	0.0594
Goodness-of-fit for the last cycle	1.240
Maximum δ/σ for last cycle	0.45

Table 3. Selected bond distances and bond angles for $(Me_3CCH_2)_3W{\equiv}CPh(py)$

A	B	Distance
W(1)	N(15)	2.575(26)
W(1)	C(2)	2.165(26)
W(1)	C(6)	2.12(3)
W(1)	C(11)	2.101(21)
W(1)	C(21)	1.74(3)

A	B	C	Angle
N(15)	W(1)	C(2)	80.8(10)
N(15)	W(1)	C(6)	77.1(10)
N(15)	W(1)	C(11)	79.7(9)
N(15)	W(1)	C(21)	179.5(10)
C(2)	W(1)	C(6)	113.4(13)
C(2)	W(1)	C(11)	116.8(14)
C(2)	W(1)	C(21)	99.6(11)
C(6)	W(1)	C(11)	119.0(14)
C(6)	W(1)	C(21)	102.7(11)
C(11)	W(1)	C(21)	100.8(11)
W(1)	C(2)	C(3)	131.1(20)
W(1)	C(6)	C(7)	128.4(23)
W(1)	C(11)	C(12)	131.5(19)
W(1)	C(21)	C(22)	174.6(20)

EXPERIMENTAL

General operating procedures and techniques have been given previously.[5] Elemental analyses were performed by Oneida Research Services, Whitesboro, New York.

Crystallographic studies

General operating procedures and listings of programs have been described previously.[7] A summary of crystal data is given in Table 2. A suitable crystal was cleaved from a larger multicrystalline conglomerate and transferred to the goniostat using standard inert atmosphere handling techniques employed by the Indiana University Molecule Structure Center and cooled to −155°C for characterization and data collection.

A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to the unique orthorhombic space group $P2_12_12_1$. Subsequent solution and refinement

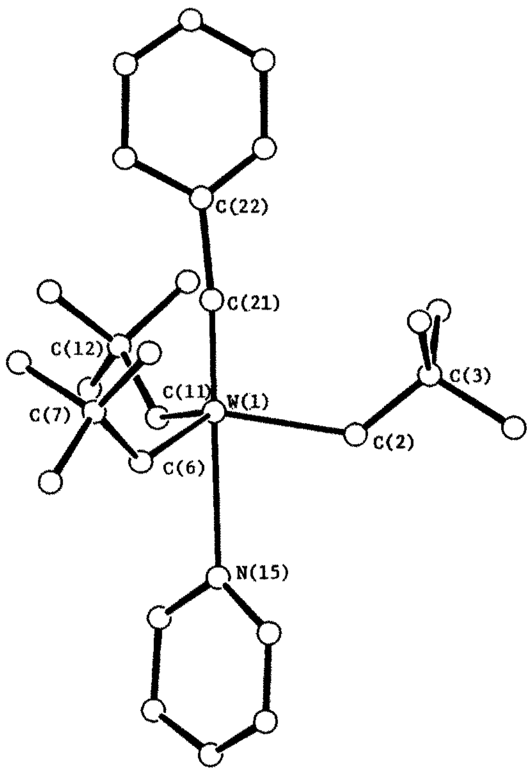

Fig. 1. A ball-and-stick drawing of the $(Me_3CCH_2)_3W\equiv CPh(py)$ molecule.

of the structure confirmed this choice. There were several weak peaks present which could not be accounted for based on the chosen cell, or a supercell based on the known cell. Some of these were identified as a second well-ordered fragment of *ca* 10% the intensity of the located cell, and other peaks indicated other fragments were possibly present. Examination of the bulk sample indicated that it would be difficult to find a more homogenous sample, so the mounted specimen was utilized.

Data were collected using a continuous θ–2θ scan with fixed backgrounds and reduced to a unique set of intensities and associated sigmas in the usual manner. The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. A difference Fourier synthesis revealed the location of some, but not all, hydrogen atoms. All hydrogen atom positions were therefore calculated using idealized geometries and d(C—H) = 0.95 Å. These calculated positions were fixed for the final cycles of refinement. The data were corrected for absorption based on measurements made on the diffractometer, but use of the absorption corrected data led to non-positive definite thermal parameters for many of the atoms. For the final cycles, the uncorrected data were used. The poor quality of the refinement is partially due to the large thermal motion present, as well as to interference from the fragments known to be present.

Chemicals

The alkylidynes $(^tBuO)_3WCR$ were made by the method of Schrock;[6b] $(CH_3)_3CCH_2Li$ and Me_3SiCH_2Li were made by published procedures. $PhCH_2MgCl$ and Me_3SiCH_2MgCl were purchased from Aldrich Chemical Co.

Preparation of $(PhCH_2)_3WC^tBu$

In a 50 cm³ Schlenk flask, $(^tBuO)_3WC^tBu$ (1.56 g, 3.3 mmol) was dissolved in Et_2O (20 cm³), the solution was cooled to 0°C and $PhCH_2MgCl$ (3.3 equiv, 2.0 M in THF) was added via syringe. After stirring for 1 h at 0°C, the volatile components were removed *in vacuo* and the residue was extracted with 4 × 10 cm³ of hexane at room temperature. The combined hexane filtrates were concentrated and cooled to *ca* −20°C for 2 days to give 1.05 g (60% yield) of $(PhCH_2)_3WC^tBu$ as yellow crystals.

$(PhCH_2)_3WC^tBu$: ^1H NMR (C_6D_6) δ: $C_6\mathit{H}_5$ 7.18 (m, 3H); 6.93 (m, 6H); 6.78 (m, 6H); $PhC\mathit{H}_2$ 1.95 (s, J_{WC} = 6.5 Hz, I = 20%, 6H); $C(C\mathit{H}_3)_3$ 1.36 (s, 9H). $^{13}C\{^1H\}$ NMR (C_6D_6) δ: $W\mathit{C}C(CH_3)_3$ 297.5 (s); C_6H_5 131.6(s); 131.1(s); 129.7(s); 127.1(s); $Ph\mathit{C}H_2$ 57.1 (s, J_{WC} = 77.1 Hz, I = 15%); $\mathit{C}(CH_3)_3$ 38.1 (s); $C(\mathit{C}H_3)_3$ 30.9 (s). IR (KBr) cm⁻¹: 2960(s); 2940(s); 2900(m); 1580(m); 1485(s); 1450(s); 1155(m); 1030(m); 1005(m); 980(m); 815(m); 800(m); 710(s); 695(s); 515(s). Found: C, 59.5; H, 5.7. Calc. for $WC_{26}H_{30}$: C, 59.3; H, 5.7%.

Preparation of $(Me_3CCH_2)_3WCSiMe_3$

A solution of $(^tBuO)_3WC(SiMe_3)$ (0.466 g, 0.96 mmol) in Et_2O (10 cm³) was cooled to 0°C and an Et_2O (5 cm³) solution of Me_3CCH_2Li (0.246 g, 3.15 mmol) was added via cannula. The mixture was stirred at 0°C for 1.5 h and the volatile components were removed *in vacuo*. Sublimation of the residue onto a water cooled cold-finger at *ca* 10^{-3} Torr and 50–55°C provided 315 mg (68% yield) of analytically pure $(Me_3CCH_2)_3WCSiMe_3$.

$(Me_3CCH_2)_3WCSiMe_3$: ^1H NMR (C_6D_6) δ: $C(C\mathit{H}_3)_3$ 1.15 (s, 27H); 0.91 (s, J_{WH} = 11.0 Hz, I = 20%, 6H); $Si(C\mathit{H}_3)_3$ 0.44 (s, J_{SiH} = 6.6 Hz, I = 8.6%, 9H). $^{13}C\{^1H\}$ NMR (C_6D_6) δ: $\mathit{C}Si(CH_3)_3$ 338.3 (s, J_{WC} = 188.7 Hz, J_{SiC} = 42.7 Hz); $^tBuCH_2$ 105.2 (s, J_{WC} = 91.7 Hz); $\mathit{C}(CH_3)_3$ 34.7(s); $C(\mathit{C}H_3)_3$ 33.9(s); $Si(\mathit{C}H_3)_3$ 1.95 (s, J_{SiC} = 41.9 Hz). IR (KBr) cm⁻¹: 2975(s); 2900(m); 2865(m); 1460(m); 1385(m); 1360(s); 1265(m); 1245(s);

1235(s); 1195(s); 1120(m); 840(s); 755(m). Found: C, 47.0; H, 8.7. Calc. for $WC_{19}H_{42}Si$: C, 47.3; H, 8.8%.

Preparation of $(Me_3SiCH_2)_3WCPh$

A solution of $(^tBuO)_3WCPh$ (0.70 g, 1.4 mmol) in Et_2O (10 cm^3) was cooled to 0°C and Me_3SiCH_2MgCl (1.0 M in Et_2O, 4.3 cm^3) was added via syringe. The mixture was stirred at 0°C for 1.5 h and the volatile components were removed *in vacuo*. The residue was extracted with 2×10 cm^3 hexane, filtered through a Celite pad and the hexane removed *in vacuo* to give $(Me_3SiCH_2)_3WCPh$ as a dark red oil. This oil could not be induced to crystallize and decomposed upon attempted sublimation/distillation but was approximately 95% pure as judged by ^1H NMR. The pyridine adduct $(Me_3SiCH_2)_3WCPh \cdot py$ was made by adding 1 cm^3 of pyridine and 5 cm^3 of DME to the oil obtained above. The dark red solution was reduced in volume by about 1/2 and cooled to -20°C overnight to give 410 mg (48% yield) of yellow–brown $(Me_3SiCH_2)_3WCPh \cdot py$ as a tacky solid.

$(Me_3SiCH_2)_3WCPh$: ^1H NMR (C_6D_6) δ: C_6H_5 7.44 (m, 2H); 7.29 (m, 2H); 6.93 (m, 1H); CH_2 0.69 (s, $J_{WH} = 9.3$ Hz, $I = 20\%$, 6H); $Si(CH_3)_3$ 0.15 (s, $J_{SiH} = 7.6$ Hz, $I = 8.0\%$, 27H). $^{13}C\{^1H\}$ NMR (C_6D_6) δ: $C(C_6H_6)$ 303.6 (s, $J_{WC} = 221.0$ Hz, $I = 14.4\%$); phenylipso 150.0 (s, $J_{WC} = 51.7$ Hz, $I = 15.1\%$); C_6H_5 130.4(s); 126.3(s); CH_2 76.2 (s, $J_{WC} = 76.4$ Hz, $I = 13.5\%$; $J_{SiC} = 40.0$ Hz, $I = 6.6\%$); $Si(CH_3)_3$ 2.7 (s, $J_{SiC} = 51.5$ Hz, $I = 7.8\%$). IR (film on NaCl) cm^{-1}; 2980(s); 2900(m); 1360(m); 1245(s); 1195(m); 945(s); 840(s); 750(s); 690(s). No analysis was attempted; compound is an oil.

$(Me_3SiCH_2)_3WCPh \cdot py$: ^1H NMR (C_6D_6) δ: C_6H_5 and py 8.89 (m, 2H); 7.65 (m, 2H); 7.38 (m, 2H); 6.96 (m, 1H); 6.92 (m, 1H); 6.67 (m, 2H); CH_2 1.17 (s, $J_{WH} = 9.1$ Hz, $I = 18\%$, 6H); $Si(CH_3)_3$ 0.21 (s, $J_{SiH} = 6.0$ Hz, $I = 8.3\%$, 27H). $^{13}C\{^1H\}$ NMR (C_6D_6) δ: C_6H_5 and py 150.5(s); 149.8(br, s); 131.5(s); 125.9(s); 124.5(br, s); CH_2 72.3 (s, $J_{WC} = 81.8$ Hz, $I = 16\%$); $Si(CH_3)_3$ 3.2(s).

Preparation of $((Me_3SiCH_2)_3W{\equiv}C)_2$

An Et_2O (10 cm^3) solution of $((^tBuO)_3WC)_2$ (0.50 g, 0.60 mmol) was cooled to 0°C and solid Me_3SiCH_2Li (0.34 g, 3.6 mmol) was added from a side arm over about 20 min. The mixture was stirred at 0°C for 3 h, and volatiles removed *in vacuo*, the residue dissolved in *ca* 3 cm^3 hexane and placed in a -20°C freezer. After about 24 h black crystals (290 mg, 52% yield) of $((Me_3SiCH_2)_3WC)_2$ were isolated by filtration and dried *in vacuo*.

$((Me_3SiCH_2)_3W{\equiv}C)_2$: ^1H NMR (C_6D_6) δ: CH_2 1.13 (s, $J_{WH} = 7.7$ Hz, $I = 22\%$, 12H); $(CH_3)_3Si$ 0.30 (s, $J_{SiH} = 6.2$ Hz, $I = 12\%$, 54H). $^{13}C\{^1H\}$ NMR (C_6D_6) δ: $W{\equiv}C$— 314.4(s); CH_2 77.8 (s, $J_{WC} = 79.4$ Hz, $I = 14.6\%$). IR (KBr) cm^{-1}: 2970(s); 2880(m); 2820(m); 1395(m); 1380(m); 1245(s); 1210(m); 940(s); 840(s); 750(s); 685(s). Found: C, 33.8; H, 7.0. Calc. for $W_2C_{26}H_{66}Si_6$: C, 34.1; H, 7.2%.

Preparation of $(Me_3CCH_2)_3WCPh \cdot py$

An Et_2O (10 cm^3) solution of $(^tBuO)_3WCPh$ (0.4 g, 0.813 mmol) was cooled to 0°C and solid Me_3CCH_2Li (0.176 g, 2.26 mmol) was added from a side arm over about 20 min. The mixture was stirred at 0°C for 1 h and the volatile components were removed *in vacuo*. The residue was dissolved in hexane (3 cm^3) at 0°C and $BF_3 \cdot OEt_2$ (0.2 cm^3, 3.25 mmol) was added via syringe to precipitate $BF_3 \cdot O^tBu^-Li^+$ as a light brown solid which was filtered off and discarded. The filtrate was reduced in volume to about 1 cm^3 and pyridine (0.2 cm^3) was added. Cooling to -20°C overnight caused 244 mg (54% yield) of $(Me_3CH_2)_3WCPh \cdot py$ to precipitate as a light brown solid.

Crystals of $((CH_3)_3CCH_3)_3WCPh \cdot py$ suitable for X-ray diffraction analysis were obtained by cooling a solution of *ca* 250 mg of the compound in *ca* 2 cm^3 of 1 : 1 hexane–pyridine to -20°C for several days.

$(Me_3CCH_2)_3WCPh \cdot py$: ^1H NMR (C_6D_6) δ: C_6H_5 and py 8.69 (m, 2H); 7.82 (m, 2H); 7.32 (m, 2H); 7.0 (m, 1H); 6.93 (m, 1H); 6.63 (m, 2H); $C(CH_3)_3$ 1.28 (s, 27H); CH_2 1.11 (s, $J_{WH} = 10.1$ Hz, $I = 25\%$, 6H). $^{13}C\{^1H\}$ NMR (C_6D_6) δ: ${\equiv}C(C_6H_5)$ 283.4 (br. s); C_6H_5 and py 150.5(s); 149.8(s); 136.8(s); 132.5(s); 125.6(s); 124.4(s); CH_2 104.2 (s, $J_{WC} = 89.2$ Hz, $I = 13.7\%$); $C(CH_3)_3$ 36.4(s); $C(CH_3)_3$ 34.6(s). IR (KBr) cm^{-1}: 2945(s); 2850(s); 1595(m); 1580(m); 1480(s); 1440(s); 1380(s); 1355(s); 1235(s); 1225(s); 1115(m); 1065(m); 940(m); 750(s); 690(s). Found: C, 57.1; H, 7.5; N, 2.4. Calc. for $WC_{27}H_{43}N$: C, 57.4; H, 7.6; N, 2.5%.

Preparation of $((Me_3CCH_2)_3WC)_2$ *and* $((Me_3CCH_2)_3WC)_2 \cdot py_2$

An Et_2O (5 cm^3) solution of $((^tBuO)_3WC)_2$ (0.875 g, 1.05 mmol) was cooled to 0°C and an Et_2O (5 cm^3) solution of Me_3CCH_2Li (0.532 g, 6.82 mmol) added via cannula. The mixture was stirred at 0°C for 1.5 h, the volume of the solution reduced by about 1/2 and placed in a −20°C freezer. After 2 days 608 mg (71% yield) of dark red $((\text{Me}_3\text{CCH}_2)_3\text{WC})_2$ was collected by filtration and dried *in vacuo*. The bis-pyridine adduct was formed by addition of excess pyridine to a suspension of $((\text{Me}_3\text{CCH}_2)_3\text{WC})_2$ in toluene and by removing the volatile components *in vacuo*.

$((\text{Me}_3\text{CCH}_2)_3\text{WC})_2$: ^{1}H NMR ($\text{C}_6\text{D}_6$) δ: $\text{C}(\text{C}H_3)_3$ 1.28 (s, 54H); $\text{C}H_2$ 1.18 (s, $J_{\text{WH}} = 9.2$ Hz, $I = 16.6\%$, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) δ: $C\text{H}_2$ 105.5 (s, $J_{\text{WC}} = 91$ Hz, $I = 15\%$); $C(\text{CH}_3)_3$ 35.9(s); $\text{C}(C\text{H}_3)$ 34.5(s). IR (KBr) cm^{-1}: 2950(s); 2895(s); 2875(s); 2750(m); 1465(m); 1360(s); 1340(s); 1230(s); 1220(m); 1105(m); 750(m); 600(m); 520(m). Satisfactory analysis not obtained.

$((\text{Me}_3\text{CCH}_2)_3\text{WC})_2\cdot\text{py}_2$: ^{1}H NMR ($\text{C}_6\text{D}_6$) δ: py 8.63 (m, 2H); 6.97 (m, 1H); 6.64 (m, 2H); $\text{C}(\text{C}H_3)_3$ 1.43 (s, 27H); $\text{C}H_2$ 1.34 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) δ: $\equiv C$— 305.3(s); py 150.0(s); 136.0(s); 124.0(s); $C\text{H}_2$ 105.3 (s, $J_{\text{WC}} = 89.8$ Hz, $I = 12.8\%$); $C(\text{CH}_3)_3$ 35.9(s); $\text{C}(C\text{H}_3)_3$ 34.5(s).

Preparation of $(\text{Me}_3\text{SiCH}_2)_3\text{WC}^t\text{Bu}$

An Et_2O (5 cm^3) solution of $({}^t\text{BuO})_3\text{WC}^t\text{Bu}$ (0.643 g, 1.4 mmol) was cooled to 0°C and $\text{Me}_3\text{SiCH}_2\text{MgCl}$ (5.0 mmol, 1.0 M in Et_2O) was added via syringe. The mixture was stirred at 0°C for 1.75 h and the volatile components were removed *in vacuo*. The residue was extracted with 2×5 cm^3 hexane and the solid filtered off and discarded. The volatile components were removed from the filtrate under a dynamic vacuum to leave a red oil that is approximately 95% pure as judged by ^{1}H NMR. Small amounts can be distilled onto a water cooled cold finger at *ca* 10^{-3} Torr and 55–60°C but, attempts to purify $(\text{Me}_3\text{SiCH}_2)_3\text{WC}^t\text{Bu}$ by short path distillation lead to decomposition.

$(\text{Me}_3\text{SiCH}_2)_3\text{WC}^t\text{Bu}$: ^{1}H NMR ($\text{C}_6\text{D}_6$) δ: $\text{C}Me_3$ 1.55 (s, 9H); $\text{C}H_2$ 0.78 (s, $J_{\text{WH}} = 9.8$ Hz, $I = 16\%$, 6H); $\text{Si}Me_3$ 0.14 (s, 27H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) δ: $\text{W}C^t\text{Bu}$ 319.5 (s, $J_{\text{WC}} = 215.0$ Hz, $I = 15\%$); $C\text{H}_2$ 74.7 (s, $J_{\text{WC}} = 78.9$ Hz, $I = 16\%$, $J_{\text{SiC}} = 40.6$, $I = 11\%$); $C(\text{CH}_3)_3$ 33.2(s); $\text{C}(C\text{H}_3)$ 32.5(s): $\text{Si}(C\text{H}_3)_3$ 2.9(s).

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Supplementary materials. Atomic positional parameters have been deposited with the Cambridge Crystallographic Data Centre.

REFERENCES

1. R. K. Viswanadham, D. J. Rowcliffe and J. Gurland (Eds), *Science of Hard Materials*. Plenum Press, New York (1983).
2. G. S. Girolami, J. A. Jensen, D. M. Pllina, W. S. Williams, A. E. Kaloyeros and C. M. Alloca, *J. Am. Chem. Soc.* 1987, **109**, 1579.
3. R. R. Schrock, *Accts Chem. Res.* 1986, **19**, 342.
4. M. H. Chisholm, D. M. Hoffman and J. C. Huffman, *Inorg. Chem.* 1983, **22**, 2903.
5. M. H. Chisholm, F. A. Cotton, M. W. Extine and R. L. Kelly, *Inorg. Chem.* 1979, **18**, 116.
6. (a) $\text{W}_2(\text{O}^t\text{Bu})_6$: M. Akiyama, M. H. Chisholm, F. A. Cotton, M. W. Extine, D. A. Haitko, D. Little and P. E. Fanwick, *Inorg. Chem.* 1979, **18**, 2266; (b) $({}^t\text{BuO})_3\text{W}{\equiv}\text{CR}$: M. L. Listemann and R. R. Schrock, *Organometalics* 1985, **4**, 74.
7. M. H. Chisholm, K. Folting, J. C. Huffman and C. C. Kirkpatrick, *Inorg. Chem.* 1984, **23**, 1021.