

Convenient Synthesis of $W(\equiv CR)X_3(dme)$ Compounds from $W(\equiv CR)(OBu^t)_3$ Triple-Bond Metathesis Products

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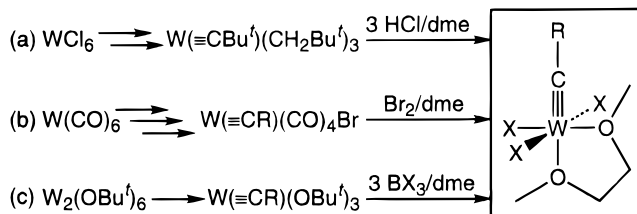
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Summary: Tungsten-alkylidyne complexes of the type $W(\equiv CR)X_3(dme)$ ($R = Bu^t, Pr^i, Ph$; $X = Cl, Br$; $dme = 1,2$ -dimethoxyethane) are prepared in 77–87% yields from reactions between $W(\equiv CR)(OBu^t)_3$ and BX_3 in the presence of dme .

Compounds of the type $M(\equiv CR)X_3(dme)$ ($M = Mo, W$; $X = Cl, Br$; $R = Me, Bu^t, CH_2Bu^t, Ph$; $dme = 1,2$ -dimethoxyethane)^{1–4} are of central importance in the chemistry of group 6 metal-alkylidyne complexes;⁵ they are key starting materials for the synthesis of a variety of high-valent^{6,7} and low-valent⁸ metal-alkylidyne compounds; they are precursors to compounds containing ligands derived from the alkylidyne moiety, including metallacyclic and cyclopentadienyl compounds,⁹ olefin-metathesis catalysts,⁷ and other derivatives;¹⁰ and they catalyze the polymerization of unsaturated substrates both in solution¹¹ and when supported on oxide surfaces.¹² Even broader applications of these compounds as synthons and catalysts could be envisioned were it

Scheme 1



not for the fact that the procedures by which they are prepared are neither general nor high yielding: the route to the widely studied compound $W(CBu^t)Cl_3(dme)$ (Scheme 1a) cannot be adapted to the preparation of derivatives with alkylidyne R groups other than *tert*-butyl and is expensive (multiple neopentyl groups are consumed en route) and time consuming (involving a difficult distillation of $W(CBu^t)(CH_2Bu^t)_3$),^{1,3} and the route to bromo derivatives of the type $W(CR)Br_3(dme)$ (Scheme 1b), while simpler and more flexible, does not provide the *tert*-butyl compounds and is unlikely to be useful for the preparation of derivatives with reactive alkylidyne R groups because it employs Br_2 as a reagent.⁴ In at least one case, the limitations imposed by these syntheses prompted the development of alternative starting materials to $M(CR)X_3(dme)$ complexes.¹³

Our interest in the synthesis and properties of conjugated materials derived from metal-alkylidyne building blocks¹⁴ led us to seek a more general synthetic route to $W(CR)X_3(dme)$ complexes. Compounds of the type $W(CR)(OR)_3$ are attractive precursors in this regard because derivatives with a wide range of alkylidyne R groups can straightforwardly be prepared by alkyne and triple-bond metathesis reactions,¹⁵ with the

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reactions between alkynes or nitriles and readily available $W_2(OBu)_6$ ¹⁶ being particularly efficient (80–90% yield) and versatile (R = alkyl, aryl, $CH=CH_2$, $C\equiv C$ ET, CN, SiMe₃, NEt₂, SBu⁺) routes to $W(CR)(OBu)_3$.^{17,18} We report herein a simple procedure for affecting this transformation: the treatment of $W(CR)(OBu)_3$ with BX_3 (X = Cl, Br) in the presence of dme provides $W(CR)X_3(dme)$ in >75% yield (Scheme 1c).

The synthesis of $W(CPh)Cl_3(dme)$ by this method is representative of those that we have investigated to date. A stirred, –78 °C solution of $W(CPh)(OBu)_3$ ¹⁷ (0.250 g, 0.51 mmol) in a mixture of pentane (20 mL) and dme (0.5 mL, 4.8 mmol) was treated with a room-temperature solution of BCl_3 (1.5 mL, 1 M in heptane, 1.5 mmol). A dark precipitate formed immediately. The reaction mixture was allowed to slowly warm to room temperature, during which time its color and appearance underwent several dramatic changes. The dark precipitate dissolved to give a bright orange solution, from which an oily brown material was subsequently deposited. The reaction was complete within 2 h, at which point the solution was colorless and the crude product was present as a purple, microcrystalline precipitate. The product was isolated by filtration and extracted into toluene. The resulting solution was filtered through Celite, reduced in volume under vacuum to ca. 3 mL, and diluted with pentane (ca. 20 mL), which induced the precipitation of microcrystalline $W(CPh)Cl_3(dme)$ (0.203 g, 0.43 mmol, 84% yield).¹⁹ The product can also be recrystallized from a concentrated toluene solution at –40 °C. Because of the air sensitivity of the starting materials and product, all manipulations were performed under a nitrogen atmosphere and solvents were rigorously dried prior to use.

This procedure can also be applied to the synthesis of related $W(CR)X_3(dme)$ compounds. Specifically, the purple compounds $W(CBu^t)Cl_3(dme)$ ^{1,3} and $W(CPr^i)Cl_3(dme)$ ²⁰ can be prepared on comparable scales under the above conditions in yields of 87% and 78%, respectively, from $W(CBu^t)(OBu)_3$ ¹⁷ and $W(CPr^i)(OBu)_3$.¹⁷ The use of BBr_3 in place of BCl_3 in this procedure provides the corresponding bromo derivatives, as demonstrated by the synthesis of the green compound $W(CPh)Br_3(dme)$ ⁴

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(18) It has been stated that this reaction “promises to make tungsten alkylidyne among the most readily available of organometallics, surpassing even Grignard reagents in their ease of preparation” (ref 1e, p 15).

(19) ¹H NMR (CD_2Cl_2 , 300.13 MHz, 25 °C): δ 7.57 (t, 2 H, Ph), 6.82 (d, 2 H, Ph), 6.74 (t, 1 H, Ph), 4.44 (s, 3 H, OCH_3), 4.15 (m, 2 H, OCH_2), 3.89 (m, 2 H, OCH_2), 3.75 (s, 3 H, OCH_3). ¹³C{¹H} NMR (CD_2Cl_2 , 75.46 MHz, 25 °C): δ 322 ($C\equiv W$), 140 (Ph), 139 (Ph), 134 (Ph), 128 (Ph), 81 (dme), 78 (dme), 73 (dme), 72 (dme). Anal. Calcd (found) for $C_{11}H_{15}Cl_3O_2W$: C, 28.14 (28.21); H, 3.22 (3.24).

from $W(CPh)(OBu)_3$ in 77% yield. Preliminary evidence suggests that this synthetic procedure will also afford more complex compounds relevant to our efforts to prepare conjugated materials from metal–alkylidyne building blocks; the reaction between 1,4- $C_6H_4\{CW(OBu)_3\}_2$ ²¹ and BCl_3/dme in 1:1 pentane/dichloromethane (the latter solvent being required to dissolve the starting material) provides a compound identified as 1,4- $C_6H_4\{CWCl_3(dme)\}_2$ ²² in 86% yield, although the poor solubility and solution-phase stability of the product have limited our efforts to fully characterize it. We are presently working to extend this methodology to derivatives with heteroatom-containing R groups and to the preparation of $Mo(CR)X_3(dme)$ compounds.

Although attempts to optimize these procedures are still in progress, we can initially note that use of fewer than 3 equiv of BX_3 is deleterious: treating $W(CPh)(OBu)_3$ with 2 equiv of BCl_3 under conditions otherwise identical to those above provides $W(CPh)Cl_3(dme)$ in 50% yield (vs 84% when 3 equiv are used), which precipitates from a yellow (on account of unreacted $W(CPh)(OBu)_3$) rather than colorless reaction mixture. The failure of the reaction to go to completion with 2 equiv of BCl_3 may be the result of the increased steric bulk and/or decreased Lewis acidity of the presumed $B(OBu)_3-xCl_x$ products of alkoxide/halide metathesis relative to those of BCl_3 or of the inherent instability of $B(OBu)_3-xCl_x$ compounds with respect to disproportionation and decomposition.²³

This simple synthesis of $W(CR)X_3(dme)$ compounds from $W(CR)(OBu)_3$ provides the derivatives available from the two previous routes to these compounds^{1,3,4} and would appear to be applicable to the synthesis of derivatives with other alkylidyne R groups as well. In addition to being a more general route to this class of compounds, this procedure also provides them in higher overall yield; $W(CBu^t)Cl_3(dme)$ and $W(CPh)Br_3(dme)$ are prepared in two steps from $W_2(OBu)_6$ (the common starting material¹⁷ for all compounds in this procedure) in overall yields of 80% (vs 50% yield from WCl_6)^{1,3} and 70% (vs 48% yield from $W(CO)_6$),⁴ respectively.

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(20) ¹H NMR (C_6D_6 , 300.13 MHz, 25 °C): δ 6.39 (t, 2 H, $CH_3CH_2CH_2CW$), 3.57 (s, 3 H, OCH_3), 3.25 (s, 3 H, OCH_3), 2.93 (m, 2 H, OCH_2), 2.84 (m, 2 H, OCH_2), 1.46 (m, 2 H, $CH_3CH_2CH_2CW$), 1.10 (t, 3 H, $CH_3CH_2CH_2CW$). ¹³C{¹H} NMR (C_6D_6 , 75.46 MHz, 25 °C): δ 332 (s, $C\equiv W$), 78 (dme), 75 (dme), 70 (dme), 60 (dme), 46 ($CH_3CH_2CH_2CW$), 28 ($CH_3CH_2CH_2CW$), 15 ($CH_3CH_2CH_2CW$). Anal. Calcd (found) for $C_8H_{17}Cl_3O_2W$: C, 22.07 (22.05); H, 3.94 (3.85).

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