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Pyranylidene Carbene Complexes from 1-Lithio 1,3-Dienes and $M(CO)_6$ (M = Cr, Mo, W): Novel Synthesis and Demetalation Reaction

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Summary: This paper reports a conceptually new and concise synthetic method leading to unprecedented, fully alkyl substituted pyranylidene carbene complexes **2** *from $M(CO)_6$ (M = Cr, Mo, W) and the readily available 1-lithio-1,3-butadiene* **1**, *bearing a leaving group, via an intramolecular trapping of metallaacylate intermediates. These carbenes have been demonstrated to have interesting and unique reactivity.*

Synthesis and demetalation of Fischer-type carbene complexes have continuously been a challenging subject in synthetic science and chemical industry.[1] Among the family of Fischer-type carbene complexes, six-membered pyranylidene carbene complexes of the group 6 metals Cr, Mo, and W have recently attracted increasing interest due to their utilizations in ring-opening reactions,[2] Diels−Alder reactions,[3] and 1,6-addition.[4] Several methods have been developed for the syntheses of pyranylidene carbene complexes;[5–8] the first report was by the reaction of cyclopropenylidene complexes with pyridinium ylides.[5] The condensation reactions of the (1-alkynyl)carbene complexes $(CO)_5M{=}C(OEt)C{\equiv}CPh$ (M = Cr, W) with carbon nucleophiles, e.g. 1,3-diketones, provided a typical route for the formation of pyranylidene carbene complexes, which bear one acyl group and two alkyl/aryl groups on the pyran ring.[6] Recently, two independent groups, Iwasawa[3b,c,4] and Uemura,[7] have reported the reaction of $M(CO)_5 \cdot L$ (M = Cr, Mo, W; L = THF, NEt_3) with β-ethynyl α,β-unsaturated

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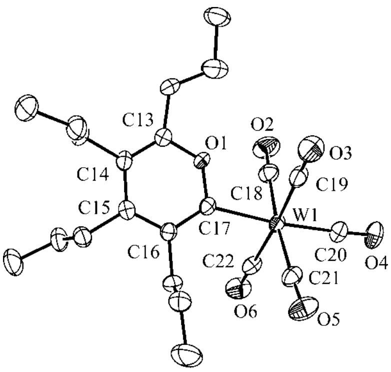
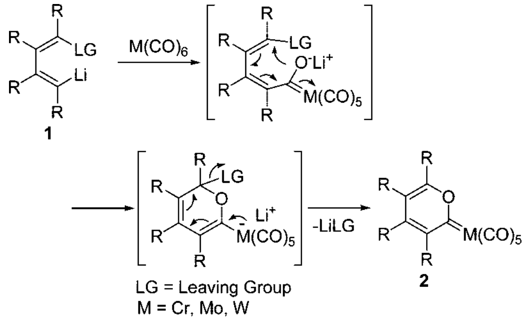


Figure 1. ORTEP drawing of **2f** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): W1−C17 = 2.236(6), C17−O1 = 1.357(7), C13−O1 = 1.357(8), C13−C14 = 1.359(9), C14−C15 = 1.433(10), C15−C16 = 1.393(9), C16−C17 = 1.407(8).

Scheme 1. Model Formation of Pyranylidene Carbene Complexes



carbonyl compounds to produce pyranylidene complexes having three substituents. Due to limitations of their synthetic methods, fully substituted pyranylidene carbene complexes have not yet been reported. Thus, more general synthetic methods for this important type of organometallic compounds are in great demand.

In this communication, we report a conceptually new and concise synthetic method leading to unprecedented fully alkyl substituted pyranylidene carbene complexes **2** from M(CO)$_6$ (M = Cr, Mo, W) and the readily available 1-lithio-1,3-butadiene **1**, bearing a leaving group, via an intramolecular trapping of metallaacylate intermediates (Scheme 1). Preliminary results of the demetalation of these carbenes will be also discussed.

4-Bromo-1-lithio-1,3-butadiene **1** was quantitatively generated in situ from its corresponding 4-bromo-1-iodo-1,3-butadiene and 2 equiv of *t*-BuLi at −78 °C for 1 h.[9] Treatment of 4-bromo-1-lithio-1,3-butadienes **1a**−**c** with 1.2 equiv of Cr(CO)$_6$ at room temperature for 3 h exclusively produced the tetrasubstituted pyranylidene carbenes **2a**−**c** in high yields (Table 1, entries 1−3). In the case of M(CO)$_6$ (M = Mo, W), the reaction with **1** required a higher temperature (60 °C) for completion in 3 h (entries 5−9). The reactions of M(CO)$_6$ (M = Cr, W) with tetrasubstituted monolithium species having five-, six-, and seven-membered rings gave exclusively the bicyclic pyranylidene carbenes **2d**,**g**−**i** in high yields (entries 4 and 7−9). The structures of **2a**,**f** have been determined by single-crystal X-ray analysis (**2f**, see Figure 1; **2a**, see the Supporting Information). To the best of our knowledge, this is the first example of the preparation of pyranylidene carbene complexes by tandem CO addition of M(CO)$_6$ (M = Cr, Mo, W) and intramolecular trapping of metallaacylate via a one-pot procedure from the readily available 1-lithio-1,3-butadienes.

X-ray structure analyses reveal that **2a**,**f** are isostructural, and only the ORTEP drawing of **2f** is shown in Figure 1.[10] The W−C$_{carb}$ bond length (2.236(6) Å) is slightly longer than those in typical tungsten pyranylidene complexes (2.177−2.228 Å).[6c,f] The C$_{carb}$−O bond length (1.357(7) Å) is slightly shorter than those in tungsten pyranylidene complexes, being in the range of 1.363−1.411 Å, [6c,f] and significantly shorter than that found in a tungsten 6-methoxy-2*H*-pyranylidene complex (1.430(7) Å).[7b] These comparisons indicate that the C$_{carb}$−O bond in **2f** displays a strong multiple bonding between the pyran oxygen and the carbene carbon.

Many attempts were made to remove the metal moiety and to transform these pyranylidene carbenes into organic products. Shown in Scheme 2 are several representative reactions demonstrating the interesting and unique reactivity of these types of pyranylidene carbene complexes. First, we found that oxidative demetalation of **2a**,**f** with I$_2$ provided 3,4,5,6-tetrapropyl-2*H*-pyran-2-one (**3**) in excellent yield (Scheme 2, path a).[11] The reaction of **2a**,**f** with elemental sulfur in the presence of NaBH$_4$ selectively generated the pyranthione complexes **4a**,**b** in quantitative yields by insertion of sulfur into the M═C (M = Cr, W) bonds, respectively (Scheme 2, path b).[12] An X-ray structure analysis of **4b** reveals that there is a C═S double bond (1.689(6) Å) and the sulfur atom is bonded coordinatively to the W(CO)$_5$ moiety (Figure 2).[10] Compound **2f** remained inert toward hydrolysis with dilute HCl; however, with 12 N HCl **2f** was hydrolyzed to yield the 2*H*-pyran **5** in 80% isolated yield (Scheme 2, path c), which was in marked contrast with the alkoxy carbene complexes that afforded aldehydes after acidolysis.[13] More interestingly, it was found that **2f** underwent a novel reductive demetalation reaction with LiAlH$_4$ to give the 3-cyclopentenone **6**, involving contraction of the six-membered ring to a five-membered ring (Scheme 2, path d).[9d,e]

In summary, the first example of tandem CO addition of M(CO)$_6$ (M = Cr, Mo, W) and intramolecular trapping of a metallaacylate intermediate has been developed to efficiently afford fully alkyl substituted pyranylidene carbene complexes from a readily available 1-lithio-1,3-butadiene and M(CO)$_6$ (M

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[10] Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. CCDC-684954 (**2a**), CCDC-684955 (**2f**), and CCDC-684956 (**4b**). Copies of these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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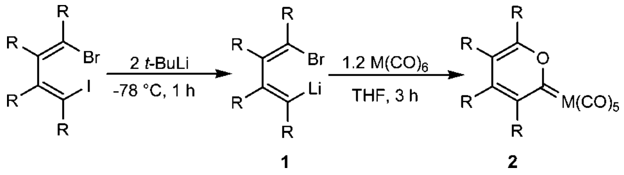
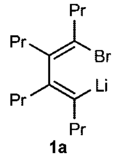
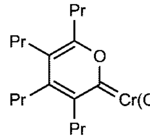
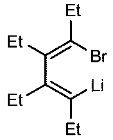
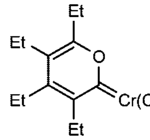
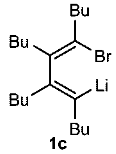
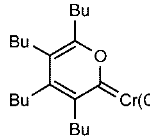
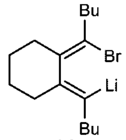
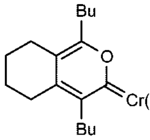
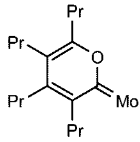
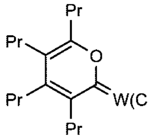
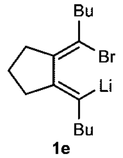
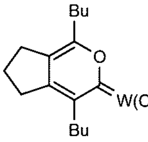
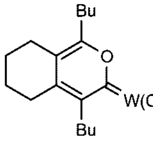
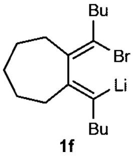
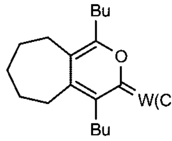
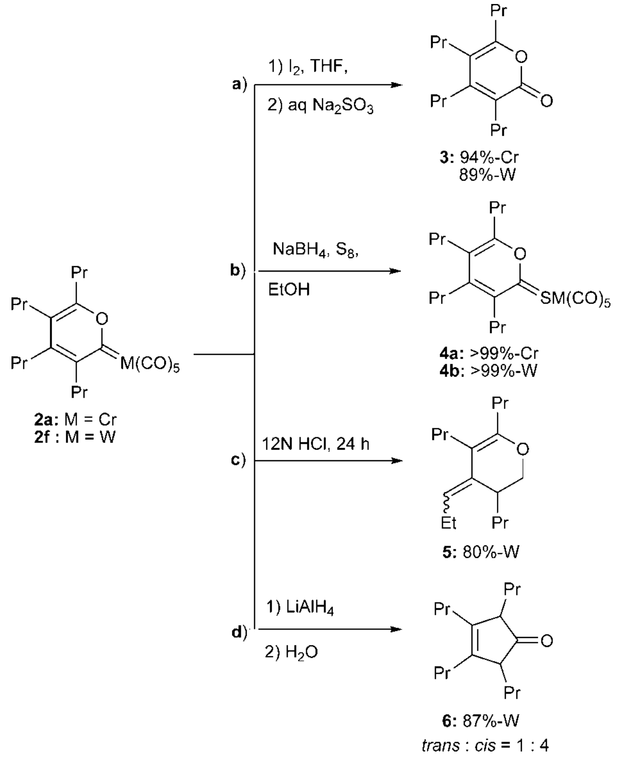
Table 1. Formation of Metal Pyranylidene Complexes from 4-Bromo-1-lithio-1,3-butadienes and Group 6 Metal Carbonyl Complexes



Entry	Lithio Reagents	M(CO)$_6$	t (°C)	Carbene **2** (Isolated Yield/%)
1	 **1a**	Cr(CO)$_6$	25	 **2a** (81)
2	 **1b**	Cr(CO)$_6$	25	 **2b** (86)
3	 **1c**	Cr(CO)$_6$	25	 **2c** (84)
4	 **1d**	Cr(CO)$_6$	25	 **2d** (73)
5	**1a**	Mo(CO)$_6$	60	 **2e** (69)
6	**1a**	W(CO)$_6$	60	 **2f** (81)
7	 **1e**	W(CO)$_6$	60	 **2g** (76)
8	**1d**	W(CO)$_6$	60	 **2h** (85)
9	 **1f**	W(CO)$_6$	60	 **2i** (82)

Scheme 2. Demetalation of Pyranylidene Carbenes 2a,f



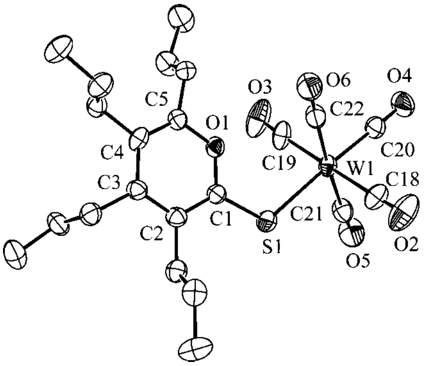


Figure 2. ORTEP drawing of **4b** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): W1−S1 = 2.558(2), C1−S1 = 1.689(6), C1−O1 = 1.355(7), C5−O1 = 1.361(8), C1−C2 = 1.393(8), C2−C3 = 1.389(9), C3−C4 = 1.436(9), C4−C5 = 1.349(8).

= Cr, Mo, W). The interesting and unique reactivity of these types of pyranylidene carbene complexes has been preliminarily demonstrated by a demetalation reaction. Further investigation into the mechanism involving a reductive demetalation reaction and into applications of this synthetic methodology and these carbene complexes are in progress.

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Supporting Information Available: Text, tables, and figures giving experimental details, X-ray data for **2a**,**f** and **4b**, and scanned NMR spectra of all products and CIF files giving crystal data for **2a**,**f** and **4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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