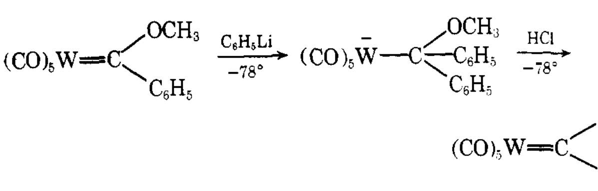
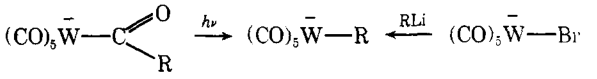
Alkyl- and Arylpentacarbonyltungsten Anions

Sir:

The carbene carbon atom in transition metal carbene complexes[1] is electrophilic and subject to attack by nucleophiles. Addition of phosphines[2] and tertiary amines[3] to the carbene carbon atom of metal carbene complexes has led to zwitterionic alkylpentacarbonyl metal complexes. Similar alkylpentacarbonylmetallate anions are presumably intermediates in the reaction of amines,[4] thiols,[5] and organolithium reagents[6,7] with metal-carbene complexes. Our interest in isolating and independently studying such species has led us to develop syntheses of alkyl- and arylpentacarbonyltungsten anions. The two routes to these previously unknown compounds[8] are shown below.





Treatment of $NEt_4^+(CO)_5W\text{-}Br^-$,[9] **1** (2.0 g, 3.75 mmol), in 40 ml of THF at room temperature with methyllithium resulted in the immediate precipitation of lithium bromide. The quantity of lithium reagent required (ca. 1.2 equiv) was determined by monitoring the disappearance of the high frequency (2068 cm^{-1}) metal carbonyl absorption in the infrared spectrum of the starting material, **1**. Addition of 10 ml of a 1 *N* sodium hydroxide solution and removal of the THF under reduced pressure gave a yellow granular solid. Recrystallization from methylene chloride-hexane yielded 1.48 g (84%) of $NEt_4^+(CO)_5WCH_3^-$, **2**.

The bright yellow crystalline compound is moderately air sensitive in the solid state and its solutions rapidly decompose upon exposure to air. The structure of **2** was assigned on the basis of its elemental analysis[10] and spectral data (Table I). The NMR spectrum of **2** exhibited an absorption at δ −0.74 relative to TMS for the methyl group bonded to tungsten. The infrared spectrum in the metal carbonyl region showed four absorptions characteristic for group VI metal pentacarbonyl anions.

The methylpentacarbonyltungsten anion, **2**, was also obtained by photolysis[11] of $N(CH_3)_4^+(CO)_5WCOCH_3^-$ [12] in acetone for 2 hr. Removal of the acetone under reduced pressure and recrystallization of the residue from methylene chloride-diethyl ether yielded **2** (10-15%).

By the same procedure as described above, reaction of **1** with phenyllithium gave the phenylpentacarbonyltungsten anion, **3**, isolated as a moderately air sensitive yellow crystalline tetraethylammonium salt (80%).[13] The NMR spectrum of **3** in the aromatic region exhibited a two-proton multiplet at δ 7.84 for the ortho protons and a three-proton multiplet at δ 6.77 for the para and meta protons. This assignment was confirmed by analysis of a 270-MHz NMR spectrum of the meta-tolyl anion, **4**, which clearly showed different chemical shifts for each of the aromatic protons (Table I). Photolysis of $NMe_4^+(CO)_5WCO(C_6H_5)^-$ [12] for 20 hr also gave the phenyl anion, **3**, isolated as the tetramethylammonium salt (25%).

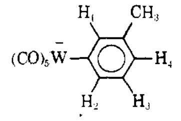
Photolysis of $NMe_4^+(CO)_5WCOCH_2Ph^-$ [14] for 6 hr gave the benzylpentacarbonyltungsten anion, **5**, isolated as a yellow crystalline tetramethylammonium salt (50%).[15] It is interesting that in the NMR spectrum of **5** the para proton appears as a multiplet at substantially higher field (δ 6.38-6.60) than the ortho and meta protons (δ 6.9-7.0). The assignment of the high field resonance to the para proton is supported by the observation of a four proton multiplet at δ 6.76 for the aromatic hydrogens of the *p*-xylylpentacarbonyltungsten anion, **6**. Reaction of **1** with benzylmagnesium chloride also gave **5**, in only 5% yield.

To assess the stability of the alkyl- and arylpentacarbonyltungsten anions and to further characterize these new compounds, reactions with electrophiles were investigated. Treatment of the compounds with HCl resulted in the instantaneous liberation of the protonated alkyl or aryl ligand in high yield. For example, reaction of the benzyl anion, **5**, with a slight excess of HCl gave toluene (94%) and $NMe_4^+(CO)_5WCl^-$ [9] isolated in 77% yield.

The reaction of **5** with $Ph_3C^{\oplus}BF_4^{\ominus}$ was also investigated in an attempt to abstract a benzylic hydride and produce a (hydridophenylcarbene)pentacarbonyltungsten(0) complex which we desired for our work on the mechanism and stereochemistry of transition metal catalyzed olefin metathesis.[16] The reaction of **5** with trityl cation yielded 1,1,1,2-tetraphenylethane in 52% and small amounts of 1,2-diphenylethane and phenyl-*p*-tolylmethane indicative of an electron transfer pathway. None of the new carbene complex or its expected decomposition products was observed.

The reaction of CO and PPh_3 with the alkyl- and arylpentacarbonyltungsten anions has been studied. Qualitatively the new compounds show a wide range of reactivities. The methyl anion, **2**, in CH_2Cl_2 was completely converted to $(CO)_5WCOCH_3^-$ in 2 days at room temperature under 1 atm of CO. The reaction of **2** with 1 equiv of PPh_3 proceeded to completion in about 15 min at room temperature to give *cis*-$(CO)_4(PPh_3)WCOCH_3^-$.[17] Under similar conditions the phenyl anion, **3**, gave analogous carbonyl inser-

Table I.

Anion	$\nu(C{=}O)$ (cm^{-1})[a]	NMR (δ)[b,c]
1 $(CO)_5\overline{W}Br$	2068(w), 1955(w), 1918(s), 1859(m)	
2 $(CO)_5\overline{W}CH_3$	2036(w), 1926(w), 1887(s), 1848(m)	−0.74(s, 3 H)WCH_3
3 $(CO)_5\overline{W}C_6H_5$	2042(w), 1940(w), 1894(s), 1856(m)	6.65−6.88 (m, 3 H) meta and para; 7.76−7.9 (m, 2 H) ortho
4[d] 	2037(w), 1937(w), 1892(s), 1857(m)	2.14(s, 3 H) CH_3-*m*; 6.57(d, 1 H, J_{43} = 7.17) H_4; 6.69 (t, 1 H, $J_{32} = J_{34}$ = 7.17)H_3; 7.63(d, 1 H, J_{23} = 7.17)H_2; 7.71 (s, 1 H)H_1
5 $(CO)_5\overline{W}CH_2C_6H_5$	2036(w), 1937(w), 1893(s), 1846(m)	2.01 (s, 2 H)WCH_2 6.38−6.60 (m, 1 H) para; 6.90−7.00 (m, 4 H) ortho and meta
6 $(CO)_5\overline{W}CH_2(C_6H_4)CH_3$-*p*	2034(w), 1932(w), 1889(s), 1840(m)	1.96(s, 2 H)WCH_2 2.14 (s, 3 H)CH_3-*p*; 6.76 (m, 4 H) ortho and meta

[a] In THF. [b] At 100 MHz recorded in acetone-d_6. [c] Resonances due to cation not shown. [d] At 270 MHz, ^1H NMR.

tion products with CO and PPh_3 but at a much slower rate than in the preceding case. The benzyl anion, **5**, under the same conditions did not yield insertion products upon treatment with either CO or PPh_3.

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(10) Anal. Calcd for $C_{14}H_{23}NO_5W$: C, 35.84; H, 4.94; W, 39.18. Found: C, 35.70; H, 4.87; W, 38.95.
(11) One and one-half grams of the acyl compound in 20 ml of acetone was photolyzed in a Srinivasan-Griffin Photochemical Reactor at 3500 Å with a stream of nitrogen bubbling through the solution. The course of the reaction was monitored by NMR.
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(15) Anal. Calcd for $C_{16}H_{19}NO_5W$: C, 39.28; H, 3.91; N, 2.86; W, 37.58. Found: C, 39.14; H, 3.96; N, 2.83; W, 37.63.
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Steric Environment of the Active Center in Metathesis of Olefins

Sir:

Since the first disclosure of olefin metathesis by Calderon[1] many catalytic systems in the homogeneous phase have been reported.[2] The oxidation state of the metal (group 6a) in the precursor complex may vary from 0 to 6. Activation of hexavalent (for tungsten) or pentavalent (for molybdenum) precursors is achieved by a great number of non-transition metal compounds such as $AlR_{3-n}Cl_n$,[1] $(n\text{-}C_4H_9)Li$,[3] $(CH_3)_4Sn$,[4] $(n\text{-}C_3H_7)MgBr$,[5] and $LiAlH_4$,[6] etc. With zerovalent precursor complexes, activation is usually obtained by means of Lewis acids.[7,8]

Due to this great variety of catalytic systems, the oxidation state as well as the coordination sphere of the active complex or complexes is unknown. We have therefore undertaken a stereochemical investigation of metathesis of *cis*-2-pentene with a great number of precursor complexes of tungsten; the purpose was to get information on the steric environment of the active catalyst or catalysts.

The major difficulty for such an approach is that metathesis of *cis*-2-pentene gives geometric isomerization of the products (2-butenes and 3-hexenes) and of the starting olefin. For highly active catalytic systems, cis–trans distribution of isomers reaches the equilibrium composition in a few minutes at room temperature. Concerning this geometric isomerization, several stereochemical studies have been reported on different systems such as: $WCl_6\text{-}C_2H_5AlCl_2\text{-}C_2H_5OH$,[9] $W(CO)_5P(C_6H_5)_3\text{-}C_2H_5AlCl_2\text{-}O_2$,[10] $L_2Mo(NO)_2Cl_2\text{-}C_2H_5AlCl_2$.[11]

From the kinetics found for these reactions, we can take for granted the fact that cis–trans isomerization is a secondary reaction of metathesis which also proceeds by a metathetic mechanism. There are good reasons to assume that both reactions occur on the same active center. Thus, the only meaningful way to characterize the steric environment of the real catalyst in metathesis is to determine the stereoselectivity at 0% conversion.

The catalytic systems used in the present work were mainly zerovalent precursor complexes of tungsten associated with $C_2H_5AlCl_2$ and sometimes molecular oxygen. We also studied a catalytic system derived from hexavalent tungsten ($WCl_6\text{-}Sn(CH_3)_4$). The solvent used was chlorobenzene in all cases. The results have been compared with various literature data related to hexavalent precursors of tungsten. In order to obtain a high accuracy concerning the trans/cis ratio of 2-butenes (C_4) and 3-hexenes (C_6) at 0% conversion, we have plotted these trans/cis ratios vs. the trans/cis ratio of 2-pentene. This gave us a linear relationship from which trans/cis C_4 and trans/cis C_6 ratios at 0% conversion have been deduced (Table I).

The fact that the same trans/cis ratios for C_4 and C_6 are obtained with all the catalytic systems used in the homogeneous phase is a very meaningful result; stereoselectivity of metathesis does not seem to depend: (1) on the electronic effects of the ligands coordinated to zerovalent precursor

Table I. Ratios (trans/cis) of 2-Butenes and (trans/cis) of 3-Hexenes for *cis*-2-Pentene Metathesis in Homogeneous Phase at 0% Conversion (at 25°C)

Catalysts[a]	Cocatalysts[a]	Trans/cis C_4[b]	Trans/cis C_6[b]
$W(CO)_6$	$C_2H_5AlCl_2$	0.69	
$W(CO)_5NH_2C_6H_{11}$		0.78	
$W(CO)_5P(n\text{-}C_4H_9)_3$		0.76	0.83
$W(CO)_5P(C_6H_5)_3$		0.73 ± 0.05[c]	0.88 ± 0.06[c]
$W(CO)_5P(OC_6H_5)_3$		0.76	0.89
$W(CO)_4(P(C_6H_5)_3)_2$-*trans*	$C_2H_5AlCl_2 + O_2$	0.77	
$W(CO)_4$(diphos)[d]	$C_2H_5AlCl_2$	0.72	
$W(CO)_3$(dien)[e]	$C_2H_5AlCl_2 + O_2$	0.69	
$W(CO)_3$(mesitylene)	$C_2H_5AlCl_2$	0.72	0.88
WCl_6[f]	$C_2H_5AlCl_2 + C_2H_5OH$	0.69	0.87
WCl_6	$Sn(CH_3)_4$[h]	0.73	
WCl_6[g]	$Li(n\text{-}C_4H_9)$	0.8 at 10% conversion	

[a] Experimental conditions: olefin/W = 100 and Al/W = 4. [b] Analysis of the gaseous phase for C_4 and of the liquid phase for C_6. [c] The uncertainty is deduced from the results of 25 experiments. [d] Diphos = bis(1,2-diphenylphosphino)ethane. [e] Dien = diethylentriamine. [f] Values obtained by plotting (trans/cis)C_4 vs. (trans/cis) C_5 from data of Calderon[9] (solvent:benzene). [g] Values obtained from data of Wang and Menapace[12] (solvent: benzene, *n*-pentane). [h] Sn/W = 1.