

Reactions of the Terminal Rhenium Acetylide Complex $\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})(\text{PPh}_3)(\text{C}\equiv\text{CH})$ and Butyllithium; Generation, Alkylation and Stannylation of Lithiocarbide Complexes of the Formula $\text{Re}(\eta^5\text{-C}_5\text{H}_4\text{X})(\text{NO})(\text{PPh}_3)(\text{C}\equiv\text{CLi})$ ($\text{X} = \text{H}, \text{Li}$)

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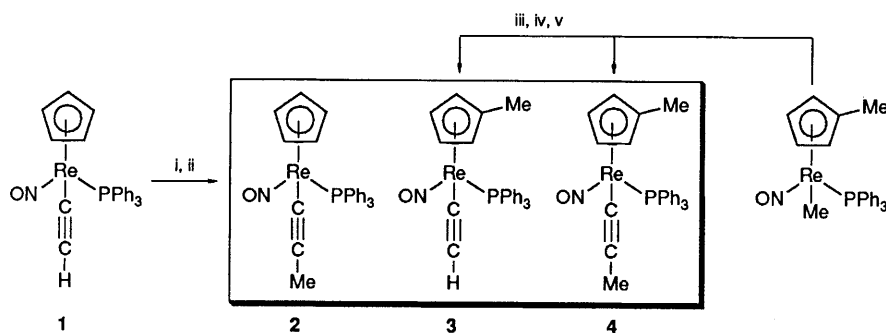
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The title reaction gives, depending upon stoichiometry and conditions, $\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})(\text{PPh}_3)(\text{C}\equiv\text{CLi})$ and $\text{Re}(\eta^5\text{-C}_5\text{H}_4\text{Li})(\text{NO})(\text{PPh}_3)(\text{C}\equiv\text{CLi})$; the first transition metal–alkali metal carbide complexes which are in turn derivatized by carbon and metal electrophiles.

Numerous terminal metal acetylide complexes, $\text{L}_n\text{MC}\equiv\text{CH}$, have been reported in the literature.^{1,2} It is also well known that organic terminal acetylenes, $\text{RC}\equiv\text{CH}$, are easily deprotonated by strong bases ($\text{p}K_{\text{BH}^+} \geq 25$).³ Thus, we sought to investigate the acid–base chemistry of the terminal rhenium acetylide complex $\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})(\text{PPh}_3)(\text{C}\equiv\text{CH})$.^{1,2} De-

protonation by an alkali metal base, $\text{M}'^+ \text{B}^-$, would afford the first example of a transition metal–alkali metal carbide complex. Such compounds should in turn be potentially valuable precursors to other unusual bimetallic C_n complexes.⁴

In order to facilitate the analysis of trapping experiments;



Scheme 1 Reactions: i, BuⁿLi; ii, MeI; iii, HBF₄·OEt₂, PhCl; iv, RC≡CH; v, BuⁿO[−]K⁺, THF

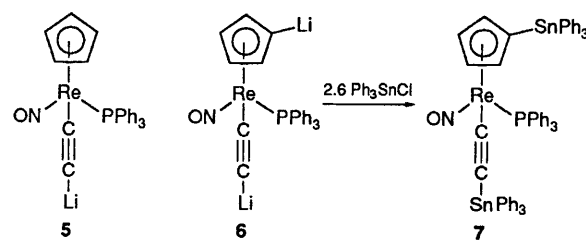
Table 1 Reactions of the acetylide complex **1** and BuⁿLi

Entry	Bu ⁿ Li	MeI addn.	Yield (%)	Product distribution (%)			
				1	2	3	4
1 ^a	1.0 equiv.	0 °C	79	8	66	0	26
2 ^a	1.5 equiv.	0 °C	89	0	46	0	54
3 ^a	2.0 equiv.	0 °C	91	0	0	0	>99
4 ^b	1.0 equiv.	20 °C	71	10	80	0	10
5 ^b	2.0 equiv.	20 °C	53	0	8	0	92

^a Solvent THF. ^b Solvent 1 : 1 THF : hexane.

authentic samples of methylated derivatives of **1** were desired. The methyl acetylide complex Re(η⁵-C₅H₅)(NO)(PPh₃)(C≡CMe), **2**, was prepared as reported previously.^{2a} The new methylcyclopentadienyl complexes Re(η⁵-C₅H₄Me)(NO)(PPh₃)(C≡CH), **3**, and Re(η⁵-C₅H₄Me)(NO)(PPh₃)(C≡CMe), **4**, were synthesized from the methyl complex Re(η⁵-C₅H₄Me)(NO)(PPh₃)(Me)⁵ via π alkyne complexes, utilizing recently reported methodology (Scheme 1).^{2b†}

A tetrahydrofuran (THF) solution of **1** was treated with 1.0 equiv. of BuⁿLi (1.7–2.7 mol dm^{−3} in hexane; freshly standardized) at −80 °C, as illustrated in Table 1, entry 1. After 1.5 h, the sample was warmed to 0 °C. Then MeI (6 equiv.) was added. Workup gave a 8:66:26 mixture of starting material **1**, the monomethylated product **2**, and dimethylated product **4** (assayed by ³¹P NMR spectroscopy; 79% yield). Accordingly, the formation of methylacetylide complexes **2** and **4** was taken as evidence for the intermediacy of lithiocarbide complexes Re(η⁵-C₅H₅)(NO)(PPh₃)(C≡CLi) **5** and Re(η⁵-C₅H₄Li)(NO)(PPh₃)(C≡CLi) **6** (Scheme 2).



Scheme 2 Lithiocarbide and stannylcarbide complexes

Parallel experiments were conducted with increasing amounts of BuⁿLi (Table 1, entries 2 and 3). With 2.0 equiv., only the dimethylated product **4** was isolated (91% yield). This shows that the dilithio complex **6** can be cleanly generated. Many other alkyl lithium bases and reaction conditions were studied in hopes of finding conditions under which only the monolithio complex **5** and monomethylated product **3** would be generated. As shown in Table 1, entry 4, better selectivity was achieved when **1** and BuⁿLi were reacted in 1:1 THF–hexane at room temperature. However, detectable quantities of **4** formed under all conditions examined.

Reactions of **1** with 1.0 and 2.0 equiv. of BuⁿLi in THF–hexane were monitored by ³¹P NMR spectroscopy. After 3 min at room temperature, the mixtures were cooled to −80 °C. The sample with 1.0 equiv. of BuⁿLi exhibited a ³¹P NMR resonance at δ 21.4; identical to that of the precursor **1**. However, addition of MeI (−80 °C) gave methylated derivatives **2** (major) and **4** (minor). The sample with 2.0 equiv. of BuⁿLi exhibited a very broad resonance at δ 24. Similar downfield shifts (3–5 ppm) have been previously observed upon lithiation of the cyclopentadienyl ligand in Re(η⁵-C₅H₅)(NO)(PPh₃)(Y) compounds.⁶ Addition of MeI (room temperature) gave **4** (>95%). These data suggest that the monolithio complex **5** has nearly the same ³¹P NMR chemical shift as **1**, whereas the dilithio complex **6** is ca. 3 ppm downfield.

Since metal C₂ complexes are of particular current interest,⁴ we sought to convert **5** or **6** to an isolable heterobimetallic derivative. Thus, **1**, BuⁿLi, and Ph₃SnCl (2.6 equiv.) were reacted in a protocol analogous to Table 1, entry 5. Workup gave the bis(stannylated) complex Re(η⁵-C₅H₄SnPh₃)(NO)(PPh₃)(C≡CSnPh₃) **7** (Scheme 2) in 49% yield.† The structure of **7** followed logically from its NMR properties [including *J*(¹³C¹¹⁹Sn) satellites], mass spectral molecular ion and microanalysis.

The above results establish that terminal acetylide ligands can be deprotonated and functionalized analogously to organic terminal acetylenes. We have previously shown that the cyclopentadienyl protons in the methyl complex Re(η⁵-C₅H₅)(NO)(PPh₃)(Me) have a pK_a (THF) of ca. 36.^{6d} Our data suggests that the acetylide proton in **1** is several pK_a units

† Selected NMR data (CDCl₃) for **3**: ¹H C₅H₄ at δ 5.41, 5.01, 4.76, 4.44 (br s), \equiv CH at 2.64 (d, *J*_{HP} 2.0 Hz), Me at 2.06 (s); ¹³C C≡C at δ 111.0 (s, C_β), 90.3 (d, *J*_{CP} 15.2 Hz, C_α), C₅H₄CH₃ at 110.2 (s), 91.5 (d, *J*_{CP} 2.0 Hz), 88.9 (s), 87.9 (s), 86.3 (d, *J*_{CP} 3.0 Hz), 14.0 (s); ³¹P δ 20.4 (s). IR (KBr) (ν/cm^{−1}): ν_{NO} 1648vs, ν_{C≡C} 1944m. Selected NMR data (CDCl₃) for **4**: ¹H C₅H₄CH₃ at δ 5.36, 4.99, 4.61, 4.37 (br s), \equiv CMe at 2.01 (d, *J*_{HP} 2.1 Hz), C₅H₄CH₃ at 1.99 (s); ¹³C C≡C at δ 119.2 (d, *J*_{CP} 1.3 Hz, C_β), 77.4 (d, *J*_{CP} 16.9 Hz, C_α), C₅H₄CH₃ at 91.1 (d, *J*_{CP} 2.4 Hz), 88.3 (s, 2C), 87.6 (s), 85.6 (d, *J*_{CP} 3.2 Hz), 13.9 (s), \equiv CCH₃ at 6.5 (d, *J*_{CP} 1.2 Hz); ³¹P δ 21.1 (s). IR (KBr) (ν/cm^{−1}): ν_{NO} 1648vs, ν_{C≡C} 2110w. Selected NMR data (C₆D₆) for **7**: ¹H C₅H₄Sn at δ 5.51, 4.95, 4.88, 4.32 (br s); ¹³C C≡C at δ 122.5 (d, *J*_{CP} 14.6 Hz, C_α), 122.4 (s, C_β), C₅H₄Sn at 105.5, 98.3, 92.9, 90.9 (s; CSn not observed); ³¹P δ 19.4 (s). IR (KBr) (ν/cm^{−1}): ν_{NO} 1655vs, ν_{C≡C} 1991m. Mass spectrum [(+)-FAB, *m/z*, centre of isotope envelope] 1266 (7⁺), 1188 (7⁺ − 78), 918 (7⁺ − SnPh₃), 842 (7⁺ − 78 − SnPh₃).

more acidic, but considerably less acidic than organic analogues. This trend follows logically from the electropositive character and π -donor properties of the $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})(\text{PPh}_3)]^+$ fragment.²

We thank the DOE for support of this research.

Received, 21st June 1991; Com. 1/03109K

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