Reactions of the Terminal Rhenium Acetylide Complex $Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(C{\equiv}CH)$ and Butyllithium; Generation, Alkylation and Stannylation of Lithiocarbide Complexes of the Formula $Re(\eta^5\text{-}C_5H_4X)(NO)(PPh_3)(C{\equiv}CLi)$ (X = H, Li)

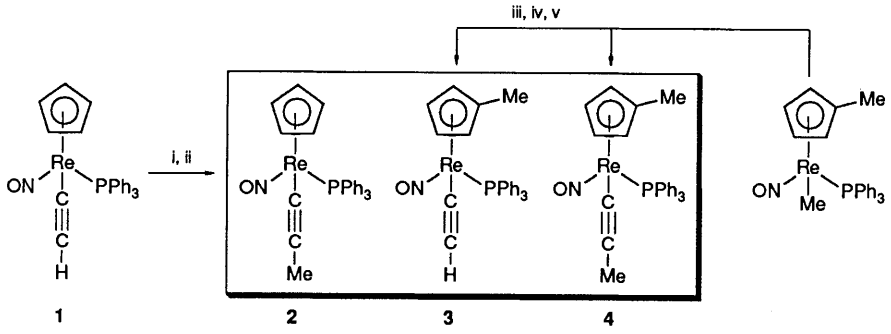
James A. Ramsden, Francine Agbossou, Dwayne R. Senn and J. A. Gladysz*

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, USA

The title reaction gives, depending upon stoichiometry and conditions, $Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(C{\equiv}CLi)$ and $Re(\eta^5\text{-}C_5H_4Li)(NO)(PPh_3)(C{\equiv}CLi)$; the first transition metal–alkali metal carbide complexes which are in turn derivatized by carbon and metal electrophiles.

Numerous terminal metal acetylide complexes, $L_nMC{\equiv}CH$, have been reported in the literature.[1,2] It is also well known that organic terminal acetylenes, $RC{\equiv}CH$, are easily deprotonated by strong bases ($pK_{BH^+} \gtrsim 25$).[3] Thus, we sought to investigate the acid–base chemistry of the terminal rhenium acetylide complex $Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(C{\equiv}CH)$ **1**.[2] Deprotonation by an alkali metal base, $M'^+ B^-$, 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, Bu^{n}Li; ii, MeI; iii, $HBF_4 \cdot OEt_2$, PhCl; iv, RC≡CH; v, Bu^{t}O$^-$K$^+$, THF

Table 1 Reactions of the acetylide complex **1** and Bu^{n}Li

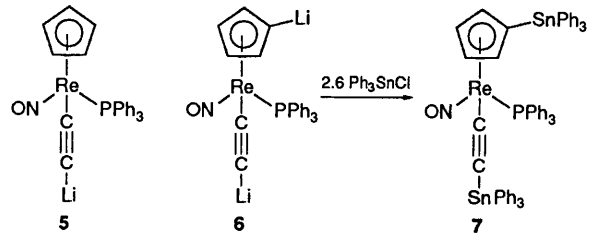
Entry	Bu^{n}Li	MeI addn.	Yield (%)	Product distribution (%) 1	2	3	4
1[a]	1.0 equiv. −80 °C, 1.5 h	0 °C	79	8	66	0	26
2[a]	1.5 equiv. −80 °C, 1.5 h	0 °C	89	0	46	0	54
3[a]	2.0 equiv. −80 °C, 1.5 h	0 °C	91	0	0	0	>99
4[b]	1.0 equiv. 20 °C, 3 min	20 °C	71	10	80	0	10
5[b]	2.0 equiv. 20 °C, 3 min	20 °C	53	0	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(η^5-C_5H_5)(NO)(PPh_3)(C≡CMe), **2**, was prepared as reported previously.[2a] The new *methyl*cyclopentadienyl complexes Re(η^5-C_5H_4Me)(NO)(PPh_3)(C≡CH), **3**, and Re(η^5-C_5H_4Me)(NO)(PPh_3)(C≡CMe), **4**, were synthesized from the methyl complex Re(η^5-C_5H_4Me)(NO)(PPh_3)(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 Bu^{n}Li (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 ^{31}P NMR spectroscopy; 79% yield). Accordingly, the formation of methylacetylide complexes **2** and **4** was taken as evidence for the intermediacy of lithiocarbide complexes Re(η^5-C_5H_5)(NO)(PPh_3)(C≡CLi) **5** and Re(η^5-C_5H_4Li)(NO)(PPh_3)(C≡CLi) **6** (Scheme 2).

† *Selected NMR data* ($CDCl_3$) for **3**: ^{1}H C_5H_4 at δ 5.41, 5.01, 4.76, 4.44 (br s), ≡CH at 2.64 (d, J_{HP} 2.0 Hz), Me at 2.06 (s); ^{13}C C≡C at δ 111.0 (s, C_β), 90.3 (d, J_{CP} 15.2 Hz, C_α), $C_5H_4CH_3$ 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); ^{31}P δ 20.4 (s). IR (KBr) (ν/cm^{-1}): ν_{NO} 1648vs, $\nu_{C\equiv C}$ 1944m. *Selected NMR data* ($CDCl_3$) for **4**: ^{1}H $C_5H_4CH_3$ at δ 5.36, 4.99, 4.61, 4.37 (br s), ≡CMe at 2.01 (d, J_{HP} 2.1 Hz), $C_5H_4CH_3$ at 1.99 (s); ^{13}C C≡C at δ 119.2 (d, J_{CP} 1.3 Hz, C_β), 77.4 (d, J_{CP} 16.9 Hz, C_α), $C_5H_4CH_3$ 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), ≡CCH_3 at 6.5 (d, J_{CP} 1.2 Hz); ^{31}P δ 21.1 (s). IR (KBr) (ν/cm^{-1}): ν_{NO} 1648vs, $\nu_{C\equiv C}$ 2110w. *Selected NMR data* (C_6D_6) for **7**: ^{1}H C_5H_4Sn at δ 5.51, 4.95, 4.88, 4.32 (br s); ^{13}C C≡C at δ 122.5 (d, J_{CP} 14.6 Hz, C_α), 122.4 (s, C_β), C_5H_4Sn at 105.5, 98.3, 92.9, 90.9 (s; CSn not observed); ^{31}P δ 19.4 (s). IR (KBr) (ν/cm^{-1}): ν_{NO} 1655vs, $\nu_{C\equiv C}$ 1991m. Mass spectrum [(+)-FAB, *m/z*, centre of isotope envelope] 1266 (**7**$^+$), 1188 (**7**$^+$ − 78), 918 (**7**$^+$ − $SnPh_3$), 842 (**7**$^+$ − 78 − $SnPh_3$).



Scheme 2 Lithiocarbide and stannylcarbide complexes

Parallel experiments were conducted with increasing amounts of Bu^{n}Li (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 Bu^{n}Li 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 Bu^{n}Li in THF–hexane were monitored by ^{31}P NMR spectroscopy. After 3 min at room temperature, the mixtures were cooled to −80 °C. The sample with 1.0 equiv. of Bu^{n}Li exhibited a ^{31}P 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 Bu^{n}Li 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(η^5-C_5H_5)(NO)(PPh_3)(Y) compounds.[6] Addition of MeI (room temperature) gave **4** (>95%). These data suggest that the monolithio complex **5** has nearly the same ^{31}P NMR chemical shift as **1**, whereas the dilithio complex **6** is *ca.* 3 ppm downfield.

Since metal C_2 complexes are of particular current interest,[4] we sought to convert **5** or **6** to an isolable heterobimetallic derivative. Thus, **1**, Bu^{n}Li, and Ph_3SnCl (2.6 equiv.) were reacted in a protocol analogous to Table 1, entry 5. Workup gave the bis(stannylated) complex Re(η^5-$C_5H_4SnPh_3$)(NO)(PPh_3)(C≡C$SnPh_3$) **7** (Scheme 2) in 49% yield.† The structure of **7** followed logically from its NMR properties [including J(^{13}C^{119}Sn) 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(η^5-C_5H_5)(NO)(PPh_3)(Me) have a pK_a (THF) of *ca.* 36.[6d] Our data suggests that the acetylide proton in **1** is several pK_a units

more acidic, but considerably less acidic than organic analogues. This trend follows logically from the electropositive character and π-donor properties of the $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)]^+$ fragment.[2]

We thank the DOE for support of this research.

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

References

1 R. Nast, *Coord. Chem. Rev.*, 1982, **47**, 89; J. P. Selegue and G. Koutsantonis, manuscript in preparation.

2 (*a*) D. R. Senn, A. Wong, A. T. Patton, M. Marsi, C. E. Strouse and J. A. Gladysz, *J. Am. Chem. Soc.*, 1988, **110**, 6096; (*b*) J. J. Kowalczyk, A. M. Arif and J. A. Gladysz, *Organometallics*, 1991, **10**, 1079.

3 J. March, *Advanced Organic Chemistry*, Wiley, New York, 3rd edn., 1985, pp. 220–222; T. Aroella, C. H. Arrowsmith, M. Hojatti, A. J. Kresge, M. F. Powell, Y. S. Tang and W.-H. Wang, *J. Am. Chem. Soc.*, 1987, **109**, 7198 and references cited therein.

4 For unsupported C_2 linkages spanning two transition metals, see: G. Kreisel, P. Scholz and W. Seidel, *Z. Anorg. Allg. Chem.*, 1980, **460**, 51; R. Nast, P. Schneller and A. Hengefeld, *J. Organomet. Chem.*, 1981, **214**, 273; R. J. Cross, M. F. Davidson and A. J. McLennan, *J. Organomet. Chem.*, 1984, **265**, C37; M. L. Listemann and R. R. Schrock, *Organometallics*, 1985, **4**, 74; M. Appel, J. Heidrich and W. Beck, *Chem. Ber.*, 1987, **120**, 1087; H. Ogawa, K. Onitsuka, T. Joh, S. Takahashi, Y. Yamamoto and H. Yamazaki, *Organometallics*, 1988, **7**, 2257; D. R. Neithamer, R. E. LaPointe, R. A. Wheeler, D. S. Richeson, G. D. Van Duyne and P. T. Wolczanski, *J. Am. Chem. Soc.*, 1989, **111**, 9056; J. Heidrich, M. Steimann, M. Apper, W. Beck, J. R. Phillips and W. C. Trogler, *Organometallics*, 1990, **9**, 1296; M. Akita, M. Terada, S. Oyama and Y. Morooka, *Organometallics*, 1990, **9**, 816; G. A. Koutsantonis and J. P. Selegue, *J. Am. Chem. Soc.*, 1991, **113**, 2316; M.-C. Chen, Y.-J. Tsai, C.-T. Chen, Y.-C. Lin, T.-W. Tseng, G.-H. Lee and Y. Wang, *Organometallics*, 1991, **10**, 378; M. St. Clair, W. P. Schaefer and J. E. Bercaw, *Organometallics*, 1991, **10**, 525.

5 J. J. Kowalczyk, A. M. Arif and J. A. Gladysz, *Chem. Ber.*, 1991, **124**, 729.

6 P. C. Heah, A. T. Patton and J. A. Gladysz, *J. Am. Chem. Soc.*, 1986, **108**, 1185; B. D. Zwick, A. M. Arif, A. T. Patton and J. A. Gladysz, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 910; G. L. Crocco and J. A. Gladysz, *Chem. Ber.*, 1988, **121**, 375; G. L. Crocco and J. A. Gladysz, *J. Am. Chem. Soc.*, 1988, **110**, 6110.