carbon monoxide under moderate conditions of temperature and pressure, employing $Ru_3(CO)_{12}$ as catalyst. We believe that the nuclearity of the catalyst is important, and we feel that this system represents one of the few examples of a cluster catalyst promoting chemistry that is not accessible from a mononuclear species.

Supplementary Material Available: A listing of pyridyl ketone products, characterization, and kinetic data (6 pages). Ordering information is given on any current masthead page.

A Versatile New Route to Carbon Complexes of the Formula $L_nMC{\equiv}CM'L'_{n'}$: Deprotonation and Metalation of the Terminal Acetylide Complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CH)$

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Received March 19, 1992

Transition metal complexes of carbon, C_x, are of interest both as models for carbide species that are generated on heterogeneous catalysts used in processing basic chemical feedstocks[1] and in the context of the many new carbon allotropes that have recently become available.[2] In particular, considerable attention has been focused upon compounds of the type $L_nM(C)_xM'L'_{n'}$, in which an unsupported C_x linkage spans two metals.[3] These furthermore show promise as nonlinear optical materials.[4] In view of the lack of general synthetic routes to such compounds, we have sought to develop rational approaches that can be adapted to different values of x.[5] Specifically, we thought that syntheses utilizing conjugate bases of terminal acetylide complexes, $L_nMC{\equiv}CH$, might offer considerable generality and flexibility. In this communication, we disclose the successful implementation of this strategy for $x = 2$.

In previous work, we found that the acetylide ligand in the cyclopentadienyl rhenium complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)$-

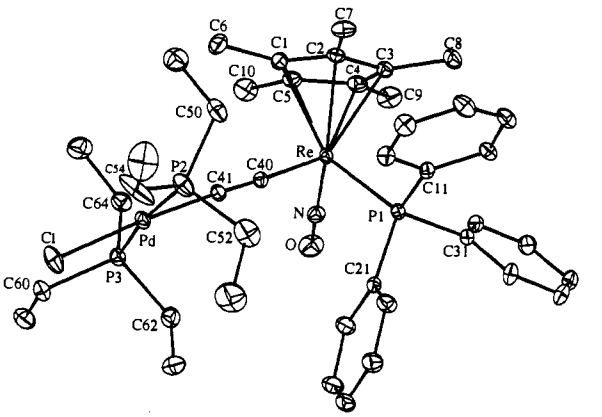
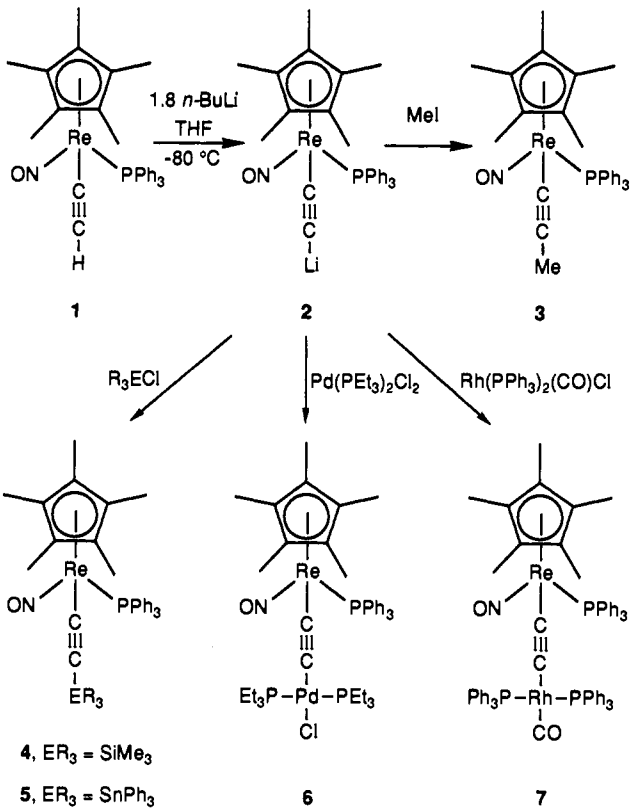


Figure 1. Molecular structure of *trans*-$(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}C)Pd(PEt_3)_2(Cl)$ (**6**). Selected bond lengths (Å) and angles (deg): Re–C40 2.079 (9), C40–C41 1.21 (1), C41–Pd 1.967 (9), Re–P1 2.359 (3), Re–N 1.750 (9), Pd–P2, 2.285 (4), Pd–P3, 2.295 (3), Pd–Cl, 2.358 (3); Re–C40–C41 173.2 (9), C40–C41–Pd 169.5 (9), C40–Re–P1, 87.1 (3), C40–Re–N, 100.5 (4), P1–Re–N 93.8 (3). Thermal ellipsoids are at the 11% level.

Scheme I. Synthesis of C_2 Complexes



$(C{\equiv}CH)$ was easily deprotonated by *n*-BuLi.[9] However, subsequent proton abstraction from the cyclopentadienyl ligand proved difficult to avoid. Thus, the *pentamethyl*cyclopentadienyl complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CH)$ (**1**)[10] was treated with *n*-BuLi (1.8 equiv/hexane) in THF at −80 °C (Scheme I). After 1.5 h, MeI (1.0 equiv) was added. Workup gave the methyl acetylide complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CMe)$ (**3**) in 95% yield. Similar reactions with Me_3SiCl and Ph_3SnCl (1.6–2.6 equiv) gave the analytically pure rhenium/group 14 C_2 derivatives $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CSiMe_3)$ (**4**) and $(\eta^5\text{-}C_5Me_5)Re$-

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(5) The most common procedures for $x = 2$ involve the deprotonation of π adducts of $L_nMC{\equiv}CH$ species.[6] However, routes featuring C≡C, CO, and σ bond metathesis,[3b,7] condensations of $L_nMC{\equiv}CH$ complexes in the presence of mild bases[3c,8a] and nucleophilic attack upon 1,2-dihaloalkynes,[8b] are also known.

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(10) Complexes **1** and **3** were prepared in a manner similar to cyclopentadienyl analogs (Kowalczyk, J. J.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1991**, *10*, 1079) and characterized as for **4**-**7**.[11]

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$(NO)(PPh_3)(C{\equiv}CSnPh_3)$ (**5**) in 86% and 45% yields, respectively. The structures of **4** and **5** followed logically from their spectroscopic properties,[11] which included mass spectral parent ions and (for **5**) ^{13}C NMR chemical shifts and J_{CSn} values diagnostic of an SnC≡C linkage.[12] Hence, the isolation of **3–5** was taken as evidence for the generation of the rhenium/lithium C_2 complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CLi)$ (**2**)—and for the versatility of **2** as an organometallic synthon.

Next, transition metal derivatives of **2** were sought. Thus, analogous reactions were conducted with the palladium and rhodium chloride complexes *trans*-$Pd(PEt_3)_2(Cl)_2$ and *trans*-$Rh(PPh_3)_2(CO)(Cl)$ (1.1 equiv).[13] Workup gave the heterobimetallic C_2 complexes *trans*-$(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}C)\text{-}Pd(PEt_3)_2(Cl)$ (**6**) and *trans*-$(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}C)Rh(PPh_3)_2(CO)$ (**7**) in 66–72% yields (Scheme I).[11] These structural assignments were supported by the phosphorus coupling patterns of the C≡C ^{13}C NMR resonances.[11] In the case of **6**, two doublets of triplets were observed, consistent with a PPh_3 ligand on rhenium and two mutually trans PEt_3 ligands on palladium. Also, **7** gave a mass spectral parent ion.

In order to verify these assignments, the crystal structure of **6** was determined (supplementary material).[14] The data, which are summarized in Figure 1, show that **6** exhibits a nearly linear ReC≡CPd linkage. The Re—C and C≡C bond lengths and Re—C≡C bond angle are similar to those found earlier[15] in the methyl acetylide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C{\equiv}CMe)$ (2.066 (7), 1.19 (1) Å, 175.8 (7)°). These values also compare closely to those in other structurally characterized $L_nMC{\equiv}CM'L'_n$ complexes,[3b,c,6a,8] including the symmetrical dirhenium species $(CO)_5ReC{\equiv}CRe(CO)_5$ (Re—C, C≡C 2.01 (2), 1.19 (3) Å; Re—C≡C 177 (2)°).[6a] Interestingly, the ethyl groups of the two PEt_3 ligands in **6** are essentially eclipsed in the solid state. A similar feature is found in the diplatinum complex *trans,trans*-$(I)(Me_3P)_2PtC{\equiv}CPt(PMe_3)_2(I)$.[8a]

Surprisingly, low-temperature ^{31}P NMR spectra of **6** and **7** showed *two* R_3PMPR_3 resonances (**6**, THF-d_8, −60 °C: 17.2/17.0 ppm, $\Delta\nu$ 20.4 Hz; **7**, CD_2Cl_2, −80 °C: 28.5/23.1 ppm, $\Delta\nu$ 555.6 Hz). These coalesced at −42 and −26 °C, respectively, giving $\Delta G^{\ddagger}(T_c)$ of 11.7 and 10.9 ± 0.2 kcal/mol[16] for the processes that render the phosphorus nuclei equivalent. We propose that these barriers arise from steric interactions between the bulky PR_3 ligands on palladium and rhodium and the pentamethylcyclopentadienyl and PPh_3 ligands on rhenium. A simple 180° rotation about one of the three σ bonds in the Re—C≡C—M linkages would then exchange the PR_3 ligands. The observation of rotational barriers involving the termini of acetylenic compounds X—C≡C—X′ appears to be extremely rare.[17]

In summary, the lithiocarbon complex **2** is the first cleanly generated transition metal counterpart of one of the most versatile classes of building blocks in synthetic organic chemistry, acetylide ions RC≡CLi. It can be anticipated that **2** and related compounds will be useful precursors to a variety of C_2 derivatives. The chemical properties of the heterobimetallic complexes **6** and **7**, and the extension of this methodology to C_3 and C_4 complexes, are under active investigation.

Acknowledgment. We thank the DOE for support of this research.

Supplementary Material Available: Listings of general crystallographic data, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **4–7** (8 pages); tables of observed and calculated structure factors for **6** (18 pages). Ordering information is given on any current masthead page.

(11) Characterization of **4–7** (microanalysis, IR, and ^1H, ^{13}C, and ^{31}P NMR) is given in the supplementary material. Selected data: IR $\nu_{C\equiv C}$ (cm^{-1}, KBr) **4** 2002, **5** 1983, **6** 1944, **7** 2017 (s-ms); $^{13}C\{^1H\}$ NMR (ppm, C_6D_6, 75 MHz) **4** 131.4 (d, J_{CP} = 15.6 Hz, ReC≡), 131.1 (s, ≡CSi), **5** 138.6 (d, J_{CP} = 15.8 Hz, J_{CSn} (satellite) = 96.4 Hz, ReC≡), 119.7 (d, J_{CP} = 1.5 Hz, ≡CSn), **6** 111.7 (dt, J_{CPPh} = 15.1 Hz, J_{CPEt} = 4.3 Hz, ReC≡), 116.2 (dt, J_{CPPh} = 1.5 Hz, J_{CPEt} = 17.5 Hz, ≡CPd), **7** 134.6 (d, J_{CP} = 10.5 Hz, ReC≡), 153.4 (dt, J_{CRh} = 37.7 Hz, J_{CP} = 21.2 Hz, ≡CRh).

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Chemical–Enzymatic Synthesis of 5′-Thio-*N*-acetyllactosamine: The First Disaccharide with Sulfur in the Ring of the Nonreducing Sugar

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Received March 11, 1992

1-Thioglycosides, with sulfur replacing oxygen in the glycosidic linkage, have been extensively described in the literature.[1] In contrast, relatively few reports exist on the synthesis and properties of 5-thioglycosides, i.e., glycosides with sulfur replacing oxygen in the ring, and only simple alkyl glycosides have been described.[2] We report here the synthesis of a glycoside of 5′-thio-*N*-acetyllactosamine (5′S-LacNAc), the first example of this latter class of oligosaccharide.

There were several compelling reasons for initiating this work. 5′S-LacNAc is a potentially important analog of LacNAc in its own right. Since such disaccharides have not been previously prepared, their conformational properties remain unknown. Should 5′S-LacNAc serve as an acceptor for other glycosyltransferases, then analogs of more complex carbohydrate antigens, such as the sialyl-Le^x tetrasaccharide,[3] could be enzymatically prepared and used in studies on protein–carbohydrate recognition. In addition to these synthetic objectives, 5′S-LacNAc, and other 5′-thio oligosaccharides, are potentially resistant to exo- or endoglycosidases.[4] They might also either be hydrolyzed by these enzymes or they might potentially be inhibitors. Since such compounds had not been previously described, these questions could not be properly addressed.

The synthetic approach used was to prepare a 5-thiosugar nucleotide in the anticipation that such an analog would act as a donor substrate for $\beta(1\rightarrow4)$galactosyltransferase (GalT), an enzyme widely used in the combined chemical–enzymatic synthesis of oligosaccharides.[5] If this were the case, the repertoire of donor

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