Table I. Crystallographic Data and Experimental and Computational Values Related to the Structure Determinations

	2-butyne·HCl	2-butyne·2HCl
mp, °C	−100 dec	−113
measuring temp, °C	−150	−170
crystal system	monoclinic	monoclinic
space group; Z	$P2_1/c$; 4	$C2/c$; 4
lattice constants		
a, Å	4.123 (2)	13.373 (7)
b, Å	13.675 (8)	7.679 (4)
c, Å	9.917 (6)	6.921 (4)
β, deg	95.56 (4)	90.47 (4)
V, Å^3	556.5 (5)	710.7 (7)
calcd density, g/cm^3	1.08	1.19
range of 2θ, deg	3–70	3–70
unique data: obsd,[a] all	1871; 2431	1318; 1573
variables in last cycle	74	44
weighting g[b]	0.0004	0.0004
R;[c] R_w[c]	0.063; 0.087	0.042; 0.055
$\Delta\rho$, e/Å^3: min; max	−0.45; 0.48	−0.46; 0.47

[a] With $|F_o| \geq 3.92\sigma_F$. [b] g in $w = 1/(\sigma_{F^2} + g|F_o|^2)$. [c] For observed reflections only.

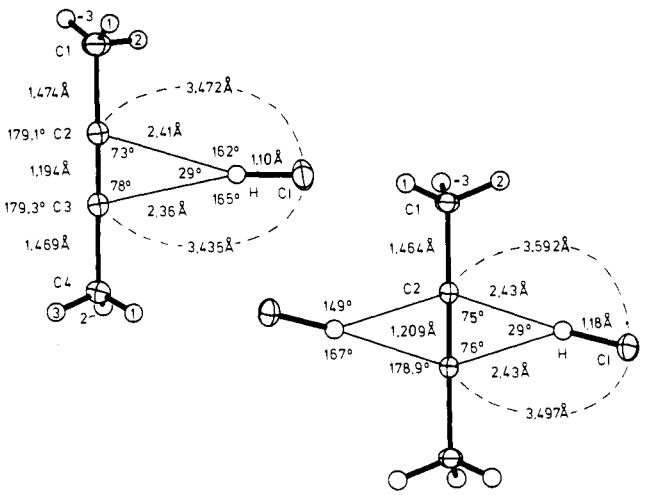

Figure 1. Solid-state molecular geometry of the complexes 2-butyne·HCl (upper left) and 2-butyne·2HCl (lower right), with interatomic distances and angles. The standard deviations, with (without) participation of the H atoms, are 0.003 (0.03–0.04) Å and 0.2° (0.4–3°) for the 1:1 complex and 0.001–0.002 (0.03) Å and 0.1° (0.3–2°) for the 1:2 complex. Projections from infinity onto the plane Cl, C2, C3 and along the crystallographic 2-fold axis, respectively; 25%-probability ellipsoids for the Cl and C atoms.

1:1 complex, but only approximately so, probably due to packing interactions, by the 1:2 complex, where *both* HCl molecules, related by a crystallographic C_2 axis across its center, approach the triple bond. The distance between the Cl atoms and the triple bond is 3.40 Å for the 1:1 complex and 3.48 Å for the 1:2 complex and thus in both cases distinctly smaller than the 3.699 Å derived for the gas-phase acetylene–HCl dimer.[1] Nevertheless, the geometry of the 2-butyne molecule appears largely undisturbed and comparable to that in the crystal structure of the alkyne alone.[10] In the 1:2 complex, the dihedral angle at the triple bond between the two Cl atoms is 112°.

Acknowledgment. Support of this work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Supplementary Material Available: Tables of atomic parameters and methyl-group geometries for 2-butyne·HCl and 2-butyne·2HCl (2 pages); listing of observed and calculated structure factors for 2-butyne·HCl and 2-butyne·2HCl (13 pages). Ordering information is given on any current masthead page.

(10) Pignataro, E.; Post, B. *Acta Crystallogr.* **1955**, *8*, 672–674.

Catalytic and Regioselective Acylation of Aromatic Heterocycles Using Carbon Monoxide and Olefins[1]

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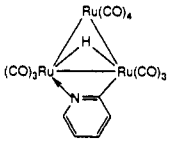
Received February 24, 1992

Many transition metal compounds are known to be excellent reagents for the selective activation of alkyl or aryl carbon–hydrogen bonds.[2] Although there are numerous examples of stoichiometric C–H bond oxidative addition to metal centers, catalytic functionalization of the C–H bond is still a relatively rare phenomenon.[3] The low catalyst turnover frequencies (ca. 0.05–4/h) observed for these catalytic reactions limit their practical utility; thus, a current challenge is to increase the rate of reaction while still maintaining high selectivity to desired products. We report our initial studies in this area using the cluster compound $Ru_3(CO)_{12}$, carbon monoxide, and olefins to catalytically acylate the ortho positions of aromatic heterocycles with extremely high regioselectivity and moderate catalyst turnover frequencies up to 300/h.

The goal of our work was to develop a method to catalytically functionalize the ortho positions of aromatic heterocycles with alkyl or acyl groups.[4] Triruthenium dodecylcarbonyl is reported to selectively activate the ortho positions in pyridine and other nitrogen-containing aromatic heterocycles to form ortho-metalated species **1**.[5]



1

It was our hope that these species might be prepared in situ and be made to react with olefins to form alkyl-substituted

(1) (a) Presented at the 198th National Meeting of the American Chemical Society, Miami Beach, FL, September, 1989. (b) Moore, E. J.; Pretzer, W. R. U.S. Patent 5,081,250 1992.

(2) (a) Hill, C. L., Ed. *Activation and Functionalization of Alkanes*; John Wiley & Sons: New York, 1989. (b) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (c) Parshall, G. W. *Chemtech* **1984**, 628. (d) Bergman, R. G. *Science* **1984**, *223*, 902. (e) Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3724. (f) Janowicz, A. H.; Bergman, R. G. *Ibid.* **1982**, *104*, 352.

(3) (a) Sakakura, T.; Sodeyama, T.; Sasaki, K.; Wada, K.; Tanaka, M. *J. Am. Chem. Soc.* **1990**, *112*, 7221. (b) Jordan, R. F.; Taylor, D. F. *Ibid.* **1989**, *111*, 778. (c) Kunin, A. J.; Eisenberg, R. *Organometallics* **1988**, *7*, 2124. (d) Marder, T. B.; Roe, C. D.; Milstein, D. *Ibid.* **1988**, *7*, 1451. (e) Gordon, E. M.; Eisenberg, R. *J. Mol. Catal.* **1988**, *45*, 57. (f) Sakakura, T.; Tanaka, M. *Chem. Commun.* **1987**, 758. (g) Burk, J. J.; Crabtree, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 8025. (h) Jones, W. D.; Kosar, W. P. *Ibid.* **1986**, *108*, 5640. (i) Baudry, D.; Ephritikhine, M.; Felkin, H.; Holmes-Smith, S. *J. Organometallics* **1983**, *2*, 161.

(4) Since we initiated this study, Jordan has reported the catalytic functionalization of substituted pyridines using cationic zirconium complexes: (a) See ref 3b. The noncatalytic functionalization of substituted pyridines has also been reported: (b) Guram, A. S.; Jordan, R. F.; Taylor, D. F. *J. Am. Chem. Soc.* **1991**, *113*, 1833. (b) Jordan, R. F.; Guram, A. S. *Organometallics* **1990**, *9*, 2116. (c) Jordan, R. F.; Taylor, D. F.; Baenziger, N. C. *Ibid.* **1990**, *9*, 1546. Furan and thiophene can be catalytically alkylated using alcohols and $RuCl_3$, but only alkylated dimers and timers were isolated: Jaouhari, R.; Guenot, P.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1986**, 1255.

(5) (a) Fish, R. H.; Kim, T.-J.; Steward, J. L.; Bushweller, J. H.; Rosen, R. K.; Dupon, J. W. *Organometallics* **1986**, *5*, 2193. (b) Bruce, M. I.; Humphrey, M. G.; Snow, M. R.; Teikink, E. R. T.; Wallis, R. C. *J. Organomet. Chem.* **1986**, *314*, 311. (c) Eisenstadt, A.; Giandomenico, C. M.; Frederick, M. F.; Laine, R. M. *Organometallics* **1985**, *4*, 2033. (d) Deeming, A. J.; Peters, R.; Hursthouse, M. B.; Backer-Dirks, J. D. *J. Chem. Soc., Dalton Trans.* **1982**, 787. The reaction of tertiary amines with $Ru_3(CO)_{12}$ has also been reported: (e) Day, M. W.; Hajela, S.; Kabir, S. E.; Irving, M.; McPhillips, T.; Wolf, E.; Hardcastle, K. I.; Rosenberg, E.; Milone, L. *Organometallics* **1991**, *10*, 2743. (f) Day, M. W.; Hajela, S.; Kabir, S. E.; Irving, M.; McPhillips, T.; Wolf, E.; Hardcastle, K. I.; Rosenberg, E.; Botta, M.; Gobetta, M.; Milone, L.; Osella, D.; Gellert, R. W. *Ibid.* **1990**, *9*, 913.

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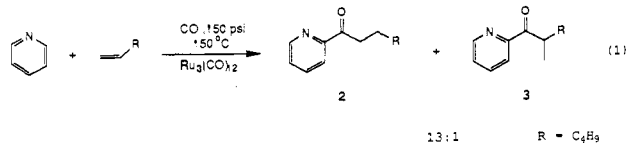
products or olefins and carbon monoxide to form acyl-substituted products. Functionalization should be specific to the ortho C–H bonds,[6] since initial coordination of the heterocycle to the ruthenium cluster is believed to proceed through nucleophilic attack of the heteroatom lone pair.

Several unsuccessful attempts were made to alkylate pyridine using 1-hexene and $Ru_3(CO)_{12}$, including thermal (180 °C) and photochemical initiation. By conducting the reaction under CO pressure, however, the pyridyl ketones **2** and **3** are produced *catalytically* with moderate turnover frequencies (ca. 160/h) (eq 1).[7] In a typical reaction, pyridine is employed as solvent and the reaction is conducted at 150 °C under 150 psi of carbon monoxide.[8] Conversion of 1-hexene to the pyridyl ketone mixture is 65% after 16 h.[9] Only ortho-substituted products are observed, making the reaction highly regioselective. In addition, no other pyridine-containing products are observed by ^1H or ^{13}C NMR spectroscopy or GC–MS.[10]



(1)

The kinetics of the acylation reaction has been examined in some detail. The reaction exhibits first-order rate kinetics with respect to pyridine and $Ru_3(CO)_{12}$ and is zero order in CO pressure (50–500 psi) and olefin concentration.[11] Good first-order rate plots were obtained, affording a pseudo-first-order rate constant of 2.6×10^{-3} s^{-1}. A possible mechanism for formation of **2** and **3** involves nucleophilic attack of pyridine on a coordinatively unsaturated metal center of the trinuclear cluster followed by pyridine coordination and ortho-metalation to afford **1**. Olefin coordination and insertion into the bridging hydride would afford two isomeric alkyl intermediates, linear and branched. Subsequent alkyl to acyl migratory insertion[12] followed by reductive elimination yields **2** and **3**. Although the kinetic analysis suggests that pyridine is involved in the rate-determining step, the data do not distinguish between pyridine coordination, C–H activation, and pyridine-induced reductive elimination.[13]

We believe that the cluster framework remains intact during the course of the acylation reaction. The possibility that mononuclear ruthenium carbonyls are responsible for the catalysis cannot be ruled out, however. The photolysis of $Ru_3(CO)_{12}$ is known to generate mononuclear fragments,[14] but pyridyl ketone products were not observed upon photolysis of the starting reaction mixture at room temperature. This result and the first-order rate dependence on the $Ru_3(CO)_{12}$ concentration lend support to a mechanism involving cluster catalysis.[15]

A number of olefins function as suitable substrates in this system. α-Olefins as small as ethylene and as large as 1-eicosene afford the corresponding linear pyridyl ketones as the major products.[16] Internal olefins such as *cis*- and *trans*-2-hexene yield the same linear/branched product ratio as terminal olefins (linear/branched = 13/1), indicating that olefin isomerization is rapid compared with pyridine acylation.[17] A single pyridyl ketone isomer can be prepared by using the hindered terminal olefin 3,3-dimethyl-1-butene, which also exhibits the fastest acylation rate of any olefin yet studied (catalyst turnover frequency = 300/h). Although unsubstituted cycloolefins such as cyclohexene react in this system, trisubstituted and tetrasubstituted olefins such as 2-methyl-2-butene and 2,3-dimethyl-2-butene do not react and are not observed to isomerize, suggesting that olefin coordination is prohibited. Olefins containing benzylic hydrogens such as *p*-methylstyrene afforded pyridyl ketone products, but heteroatom-containing olefins (e.g., butyl vinyl ether) and acetylenes afford low yields of complex product mixtures.

The reactivity of alkyl-substituted pyridines having at least one ortho carbon–hydrogen bond is comparable to that of pyridine. However, when no ortho carbon–hydrogen bonds are present, as in 2,6-lutidine, acylation of the heterocycle is not observed, consistent with the finding that only the ortho positions are activated. Heterocycles containing the pyridine substructure (e.g., quinoline) react, but at a much slower rate compared to that of pyridine. The oxygen- and sulfur-containing heteroaromatics furan and thiophene are not reactive, undoubtedly a consequence of the weak nucleophilic character of these molecules. The lack of reactivity observed for 4-chloropyridine, in which the heteroatom is deactivated by the electronegative chlorine atom, further illustrates the importance of the nucleophilicity of the heteroatom-containing substrate.

A variety of other transition metal carbonyl compounds were investigated for their ability to catalyze this acylation reaction. None of the other simple carbonyl clusters (e.g., $Fe_3(CO)_{12}$, $Os_3(CO)_{12}$, $Rh_4(CO)_{12}$, $Re_2(CO)_{10}$) were found to be active. $Os_3(CO)_{12}$ is known to form pyridyl–hydride compounds analogous to **1**,[18] but the stability of the osmium analogue may preclude catalytic activity. The monophosphine complex $Ru_3(CO)_{11}(PPh_3)$ was found to be much less active in catalyzing the acylation reaction than the parent carbonyl, and no activity was observed for the triphosphine complex $Ru_3(CO)_9(PPh_3)_3$. Pyridyl–hydride compound **1** has been prepared separately and found to be catalytically active, but control experiments in the absence of olefin establish that **1** decomposes to $Ru_3(CO)_{12}$ and pyridine under the conditions of the acylation reaction.

We have shown that pyridine and other nitrogen-containing aromatic compounds can be ortho-acylated using olefins and

(6) It is known that N-alkylation of pyridine activates both the C-2 and C-4 positions toward nucleophilic attack (although in this system the C-4 position is not accessible to intramolecular attack). House, H. O. *Modern Synthetic Reactions*; W. A. Benjamin: New York, 1972; pp 74, 75.

(7) Pyridyl ketones have been prepared by the stoichiometric reaction of pyridinecarbonitriles with alkylmagnesium reagents. (a) Reimann, E.; Ziegon, H.-L. *Justus Liebigs Ann. Chem.* **1976**, 1351. (b) Teague, P. C.; Ballentine, A. R.; Rushton, G. L. *J. Am. Chem. Soc.* **1953**, *75*, 3429.

(8) For a typical reaction, a solution of $Ru_3(CO)_{12}$ (0.053 mmol) and 1-hexene (4.0 mmol) in pyridine (15 mL) was placed in a pressure vessel, which was then charged with CO (150 psi) and heated at 150 °C with rapid stirring. The reaction can be performed under 1 atm of CO, but yields are significantly reduced.

(9) Addition of **2** to a solution of $Ru_3(CO)_{12}$ and 1-heptene in pyridine was found to inhibit the formation of 1-(2-pyridyl)-1-octanone as well as the isomerization of 1-heptene to internal isomers. Coordination of the pyridyl ketone product to the cluster (possibly via chelation through the N and O atoms) may account for the rapid decline in rate (after 1 h) as the product concentration increases during the course of the reaction.

(10) The ^1H NMR spectral data of **2** are consistent with literature reports for the same compound prepared by stoichiometric methods (see ref 6a). Small amounts of the disubstituted product, 2,6-bis(1-oxopropyl)pyridine, are observed when ethylene is employed as the olefin substrate.

(11) Kinetic experiments were performed in toluene solvent at 150 °C using 1-hexene as the olefin substrate with $[Ru_3(CO)_{12}] = 2.5$ mM. Similar results were obtained when 3,3-dimethyl-1-butene was employed as the olefin.

(12) Although carbonylation of the ortho-metalated pyridine followed by reductive elimination is a possible alternative, carbonylation of **1** has not been reported whereas simple acyl derivatives (i.e., COR) of $Ru_3(CO)_{12}$ are known. Azam, K. A.; Deeming, A. J.; Rothwell, I. P. *J. Chem. Soc., Dalton Trans.* **1981**, 91. Johnson, B. F. G.; Lewis, J.; Odiaka, T. I.; Raithby, P. R. *J. Organomet. Chem.* **1981**, *216*, C56.

(13) Control experiments using pyridine-d_0, pyridine-d_5, and 3,3-dimethyl-1-butene establish that orthometalation is reversible under conditions of the acylation reaction. Deuterium scrambling into the methyl positions of 3,3-dimethyl-1-butene was not observed.

(14) (a) Johnson, B. F. G.; Lewis, J.; Twigg, M. V. *J. Organomet. Chem.* **1974**, *67*, C75. (b) Yarrow, P.; Ford, P. C. *Ibid.* **1981**, *214*, 115. (c) Desrosiers, M. F.; Wink, D. A.; Trautman, R.; Friedman, A. E.; Ford, P. C. *J. Am. Chem. Soc.* **1986**, *108*, 1917.

(15) For review of transition metal cluster complexes in catalysis, see: (a) Darensbourg, D. J. *Uses of Metal Clusters in Homogeneous and Heterogeneous Catalysis.* In *Metal-Metal Bonds in Clusters and Chemical Catalysis*, Proceedings of the Indiana University Coop Chemistry Program, John P. Plenum: New York, 1990; p 41. (b) Smith, A. K.; Basset, J. M. *J. Mol. Catal.* **1977**, *2*, 229.

(16) Branched ketone compounds are also observed as minor constituents (7–10%) in the ketone product mixture.

(17) The ratio of *cis*-2-hexene to *trans*-2-hexene and the ratio of linear to branched pyridyl ketone products remained constant regardless of the starting olefin employed.

(18) (a) Yin, C. C.; Deeming, A. J. *J. Chem. Soc., Dalton Trans.* **1975**, 2091. (b) Burgess, K.; Holden, H. D.; Johnson, B. F. B.; Lewis, J.; Hursthouse, M. B.; Walker, N. P. C.; Deeming, A. J.; Manning, P. J.; Peters, R. *Ibid.* **1985**, 85.

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 $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)$-

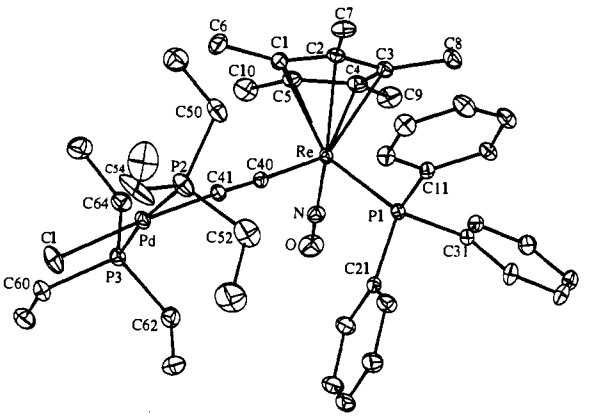
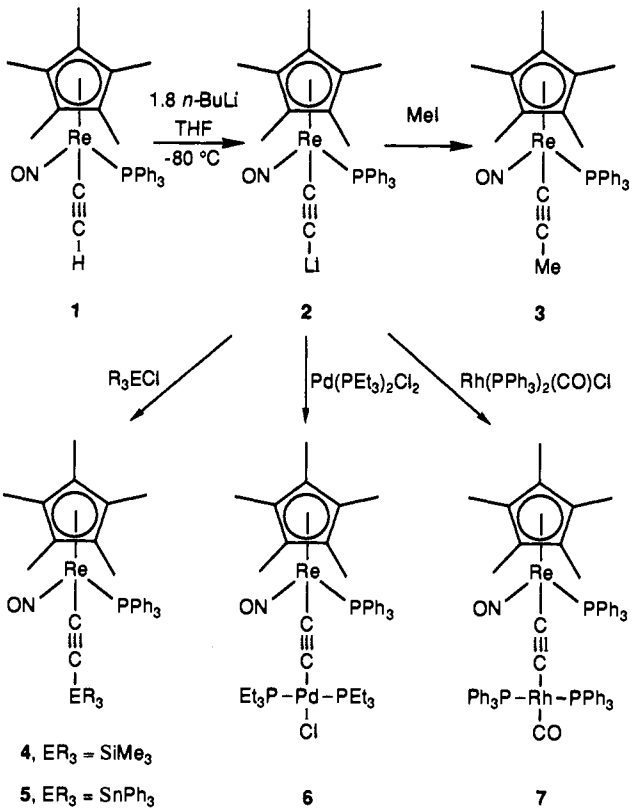


Figure 1. Molecular structure of *trans*-$(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}C)Pd(PEt_3)_2(Cl)$ (**6**). Selected bond lengths (Å) and angles (deg): Re-C40 2.079 (9), C40-C41 1.21 (1), C41-Pd 1.967 (9), Re-P1 2.359 (3), Re-N 1.750 (9), Pd-P2, 2.285 (4), Pd-P3, 2.295 (3), Pd-Cl, 2.358 (3);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

(1) (a) Anderson, R. B. *The Fischer-Tropsch Synthesis*; Academic Press: Orlando, FL, 1984. (b) Pines, H. *The Chemistry of Catalytic Hydrocarbon Conversions*; Academic Press: Orlando, FL, 1981; cf. pp 188, 208.

(2) Kroto, H. W.; Allaf, A. W.; Balm, S. P. *Chem. Rev.* **1991**, *91*, 1213.

(3) Leading references follow. (a) C_1: Etienne, M.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1991**, *113*, 2324. (b) C_2: Koutsantonis, G. A.; Selegue, J. P. *Ibid.* **1991**, *113*, 2316. (c) C_2: Lemke, F. R.; Szalda, D. J.; Bullock, R. M. *Ibid.* **1991**, *113*, 8466. (d) C_4: Wong, A.; Kang, P. C. W.; Tagge, C. D.; Leon, D. R. *Organometallics* **1990**, *9*, 1992. (e) C_4: Fyfe, H. B.; Mlekuz, M.; Zargarian, D.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1991**, 188.

(4) Lewis, J.; Khan, M.; Kakkar, A. K.; Johnson, B. F. G.; Marder, T. B.; Fyfe, H. B.; Wittmann, F.; Friend, R. H.; Dray, A. E. *J. Organomet. Chem.* **1992**, *425*, 165 and references therein.

(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.

(6) (a) Appel, M.; Heidrich, J.; Beck, W. *Chem. Ber.* **1987**, *120*, 1087. Heidrich, J.; Steimann, M.; Appel, M.; Beck, W.; Phillips, J. R.; Trogler, W. C. *Organometallics* **1990**, *9*, 1296. (b) Akita, M.; Terada, M.; Oyama, S.; Moro-oka, Y. *Ibid.* **1990**, *9*, 816. (c) Frank, K. G.; Selegue, J. P. *J. Am. Chem. Soc.* **1990**, *112*, 6414.

(7) (a) Listeman, M. L.; Schrock, R. R. *Organometallics* **1985**, *4*, 74. (b) Neithamer, D. R.; LaPointe, R. E.; Wheeler, R. A.; Richeson, D. S.; van Duyne, G. D.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1989**, *111*, 9056. (c) St. Clair, M.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1991**, *10*, 525. (d) Caulton, K. G.; Cayton, R. H.; Chisholm, M. H.; Huffman, J. C.; Lobkovsky, E. B.; Xue, Z. *Ibid.* **1992**, *11*, 321.

(8) (a) Ogawa, H.; Onitsuka, K.; Joh, T.; Takahashi, S.; Yamamoto, Y.; Yamazaki, H. *Organometallics* **1988**, *7*, 2257. (b) Davies, J. A.; El-Ghanam, M.; Pinkerton, A. A.; Smith, D. A. *J. Organomet. Chem.* **1991**, *409*, 367.

(9) Ramsden, J. A.; Agbossou, F.; Senn, D. R.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1991**, 1360.

(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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