Table II. Relevant Bond Distances (Å) and Angles (deg) within Compound **3**, Defining the Carbonyl Stereochemistry[a]

pocket	$(CO_{ax}ReCO_{eq})_2$	$Re–Re–C_{eq}$	$Re–Re–C_{ax}$	$C–Re–C$	$Re–Re$
a	C13, Re1, C11–C24, Re2, C22	93.2, 93.1	89.7, 92.4	92.0, 91.0	3.456
b	C14, Re1, C11–C23, Re2, C22	93.2, 93.1	88.8, 86.4	89.5, 91.7	3.456
c	C13, Re1, C12–C23′, Re2′, C21′	88.2, 86.7	89.5, 89.0	90.1, 91.2	3.422
d	C14, Re1, C12–C24′, Re2′, C21′	88.2, 86.7	88.2, 89.5	91.3, 90.4	3.422

[a] Typical esd's are Re–Re–C 0.03°, C–Re–C 0.04°, and Re–Re 0.001 Å. The ′ refers to the $-x$, $-y$, $-z$ symmetry operation.

to $[Re_4H_4(CO)_{15}]^{2-}$ [10g] and to $[Re_4C(CO)_{15}I]^-$,[10h] which adopt, however, a spiked triangle and a folded-square geometry, respectively.

A comparison of the structural features of the three title compounds shows a similar arrangement of the carbonyl ligands around each metal center (two equatorial and two axial) and a definite similarity of the metal carbonyl interactions (the $Re–C_{eq}$ being shorter than the $Re–C_{ax}$). On the contrary, the Re–Re distances (2.876 Å in **1**, 3.244, 3.240, and 3.238 Å in **2**, and 3.456 and 3.422 Å in **3**) show all the wide flexibility of the $M(\mu-H)M$ systems. The hydride ligands have been reasonably located and refined for the dimeric and the trimeric species, but the presence of many spurious peaks in the last difference Fourier map (also when computed with the low-angle reflections only) did not allow their unambiguous location and refinement in $[Re_4(\mu-H)_4(CO)_{16}]$. The fully eclipsed carbonyl conformation and the long Re–Re edges suggest the presence of four "linear, eclipsed" M–H–M three-center two-electron bonds,[11] similar to those found in some $[(CO)_5MHM(CO)_5]^-$ dimers (M = Cr, Mo, W),[12] which, despite the linearity of the $C_{ax}–M\cdots M–C_{ax}$ axis, have M–H–M moieties markedly bent and staggered, with respect to the nearest carbonyls.[12e] A truly linear M–H–M system would therefore be unprecedented; thus, for lack of other evidence, we prefer to consider the four H ligands slightly off axis, with a Re–H bond distance of ca. 1.82 Å, as found from the neutron diffraction study of $[Re_3(\mu-H)_3(CO)_{11}(PPh_3)]$.[4] In this hypothesis each H atom can bridge a Re–Re edge in two different ways: (i) from inside the metal cluster, in the Re atoms' plane, (ii) from the outside, below or above the metal atoms' plane, in staggered conformation with respect the adjacent carbonyls. On the basis of atom pair potential energy computations, the four internal sites are the less hindered, but cannot be all simultaneously occupied, because of the hydrogen–hydrogen repulsion.[13] This implies that at least two hydrogen atoms must be in the external sites, likely in pockets a and a′, defined in Table II (primes refer to the equivalent, symmetry-related, pockets or atoms), because the analysis of the Re–Re–C and C–Re–C angles for the four symmetry-independent

external $(CO_{ax}ReCO_{eq})_2$ pockets shows the expansion of site a at the expense of the other three. Thus, while in solution the presence of a single hydridic resonance (in the ^{1}H NMR spectrum) indicates a highly symmetric structure (D_{4h}) or the occurrence of some process equalizing the hydrides, we suggest for **3**, in the solid state, the structure reported in Figure 1c, of C_{2h} overall symmetry.

Square-planar metal cluster compounds are uncommon. There are a few examples: for instance $[Re_4C(CO)_{15}I]^-$ (stabilized by a semiinterstitial carbide),[10h] $Pt_4(CH_3CO_2)_8$[14] (stabilized by the bridging acetate groups), and $Os_4(CO)_{16}$ (unsupported and not very stable).[15] Lauher[16] suggested that within D_{4h} symmetry only two good bonding metal–metal interactions are allowed and thus an unsupported square metal cluster should be unstable; recently this view has been questioned.[17] Moreover, the presence of four hydrides dramatically changes the situation[18] and indeed $[Re_4(\mu-H)_4(CO)_{16}]$ appears somewhat stable.

Supplementary Material Available: Perspective view of **3** and tables of fractional atomic coordinates, anisotropic thermal factors, and bond distances and angles for **1·2** and **3** (19 pages); listing of observed and calculated structure factors for **1·2** and **3** (41 pages). Ordering information is given on any current masthead page.

(14) Carrondo, M. A. A. F. de C. T.; Skapski, A. C. *Acta Crystallogr.* **1978**, *B34*, 1857.

(15) Johnston, V. J.; Einstein, F. W. B.; Jones, R. H.; Pomerory, R. K. *J. Am. Chem. Soc.* **1987**, *109*, 8111.

(16) Lauher, J. W. *Int. J. Quantum Chem.* **1988**, *22*, 309.

(17) Mealli, C.; Proserpio, D. M. *J. Am. Chem. Soc.*, in press.

(18) Even in the hypothesis of D_{4h} symmetry, that is with all the hydrides in the metal plane, HEMO calculations show that the presence of the four hydrogen orbitals allows the formation of four good M–H–M bonds. Moreover, the reduction of symmetry associated with the location of two H atoms out of the metals plane further removes the symmetry constraints to orbital's mixing.[16]

Spectroscopic and Chemical Evidence for the Reversible Formation of Vinylcopper Intermediates in the Stannylcupration of Terminal Alkynes

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The stannylcupration of 1-alkynes is an efficient and widely used route to vinylstannanes.[1,2] In spite of its synthetic utility, the mechanism of this reaction is still poorly understood. The most widely accepted hypothesis, advanced by Piers, suggests that

(10) (a) $[Re_4(\mu-H)_4(CO)_{12}]$, doubly unsaturated tetrahedron, 56 CVEs: Wilson, R. D.; Bau, R. *J. Am. Chem. Soc.* **1976**, *98*, 4687. (b) $[Re_4(\mu-H)_3(\mu_3-H)_2(CO)_{12}]^-$, unsaturated tetrahedron, 58 CVEs: Beringhelli, T.; D'Alfonso, G.; Ciani, G.; Molinari, H. *J. Chem. Soc., Chem. Commun.* **1987**, 486. (c) $[Re_4(\mu-H)_6(CO)_{12}]^{2-}$, tetrahedron, 60 CVEs: Kaesz, H. D.; Fontal, B.; Bau, R.; Kirtley, S. W.; Churchill, M. R. *J. Am. Chem. Soc.* **1969**, *91*, 1021. Ciani, A.; Sironi, A.; Albano, V. G. *J. Organomet. Chem.* **1977**, *136*, 339. (d) $[Re_4(\mu-H)_4(CO)_{13}]^{2-}$, tetrahedron, 60 CVEs: Bertolucci, A.; Ciani, G.; Freni, M.; Romiti, P.; Sironi, A. *J. Organomet. Chem.* **1976**, *117*, C37. (e) $[Re_4(CO)_{16}]^{2-}$, rhombic, 62 CVEs: Bau, R.; Kaesz, H. D.; Fontal, B.; Churchill, M. R. *J. Am. Chem. Soc.* **1967**, *89*, 6374. (f) $[Re_4(\mu-H)_5(CO)_{14}]^-$, butterfly, 62 CVEs: Beringhelli, T.; Ciani, G.; D'Alfonso, G., De Maldé, V.; Sironi, A.; Freni, M. *J. Chem. Soc., Dalton Trans.* **1986**, 1051. (g) $[Re_4H-(\mu-H)_3(CO)_{15}]^{2-}$, spiked triangle, 64 CVEs: Ciani, G.; Albano, V. G.; Immirzi, A. *J. Organomet. Chem.* **1976**, *121*, 237. (h) $[Re_4(\mu_4-C)(CO)_{15}I]^-$, folded square, 64 CVEs: Beringhelli, T.; Ciani, G.; D'Alfonso, G.; Sironi, A.; Freni, M. *J. Chem. Soc. Chem. Commun.* **1985**, 978.

(11) Teller, R. G.; Bau, R. *Struct. Bonding* **1981**, *44*, 1.

(12) (a) Roziere, J.; Williams, J. M.; Stewart, R. P.; Petersen, J. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1977**, *99*, 4497. (b) Petersen, J. L.; Brown, R. K.; O'Connor, J.; Dahl, L. F.; Williams, J. M. *Inorg. Chem.* **1978**, *17*, 3460. (c) Petersen, J. L.; Brown, R. K.; Williams, J. M.; McMullan, R. K. *Inorg. Chem.* **1979**, *18*, 3493. (d) Petersen, J. L.; Brown, R. K.; Williams, J. M. *Inorg. Chem.* **1981**, *20*, 158. (e) Hart, D. W.; Bau, R.; Koetzle, T. F. *Organometallics* **1985**, *4*, 1590.

(13) Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2509. HYDEX located 12 (of which only 6 are symmetry independent) potential energy (PE) minima; the four internal locations have a PE of 0.1, while pockets (a,a′), (b,b′), (c,c′), and (d,d′) have a PE of 3.9, 4.9, 7.2, and 7.7 (arbitrary units), respectively (for a Re–H bond distance of 1.85 Å). When the H···H pair potential is added and the H locations refined, the best configuration has two internal and two external (pockets a and a′) hydrogen atoms (see Figure 1c).

(1) (a) Piers, E.; Chong, J. M. *J. Chem. Soc., Chem. Commun.* **1983**, 934–935. (b) Piers, E.; Morton, H. E.; Chong, J. M. *Can. J. Chem.* **1983**, *65*, 78–87. (c) Piers, E.; Chong, J. M. *Can. J. Chem.* **1988**, *66*, 1425–1429. (d) Cox, S. D.; Wudl, F. *Organometallics* **1983**, *2*, 184–185. (e) Westmijze, H.; Ruitenberg, K.; Meijer, J.; Vermeer, P. *Tetrahedron Lett.* **1982**, 2797–2798. (f) Zweifel, G.; Leong, W. *J. Am. Chem. Soc.* **1987**, *109*, 6409–6412.

(2) For a list of leading references, see: Sharma, S.; Oehlschlager, A. C. *J. Org. Chem.* **1989**, *54*, 5064–5073.

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Communications to the Editor

this reaction proceeds via reversible addition to yield equilibrium mixtures of alkyne and adduct which may be driven to product by the presence of a protic solvent that hydrolyzes the presumptive vinylcopper intermediate but not the stannylcuprate.[1a-f] Low product yields in the absence of a proton source have been attributed to an unfavorable alkyne–adduct equilibrium.[1a] While providing a plausible working hypothesis, this mechanism has remained speculative due to the lack of experimental evidence for the putative organocopper intermediate. We now report ^{2}H and ^{13}C NMR spectroscopic and chemical evidence that cuprate 1 [Bu$_3$SnCu(CN)Li·2LiCl] reacts with 1-alkynes via completely reversible processes to yield solutions in which the adducts are favored over starting materials.[3] Remarkably these reactions do not occur at appreciable rates below –30 °C.

Bu$_3$SnCu(CN)Li·2LiCl
1
or
(Bu$_3$Sn)$_2$Cu(CN)Li$_2$
2

[1]
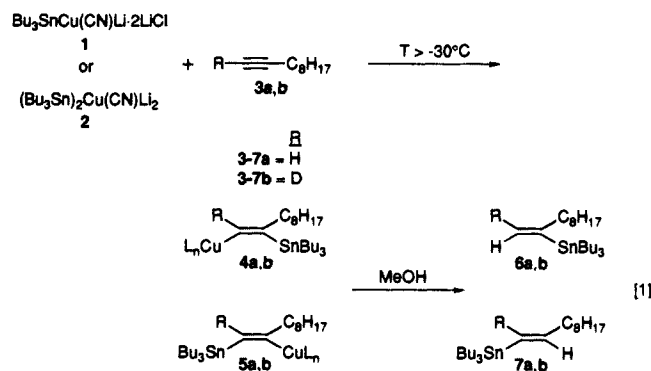
Monitoring solutions of **1** or **2** [(Bu$_3$Sn)$_2$Cu(CN)Li$_2$] and 1-decyne (**3a**) over the temperature range –78 to 0 °C by ^{13}C NMR spectroscopy revealed no reaction below –35 °C. Warming above –30 °C resulted in the gradual disappearance of the signals attributable to the sp carbons of **3a** (70.9 and 85.0 ppm) with concomitant emergence of four new downfield signals at 129.7, 159.0, 170.8, and 200.3 ppm. The chemical shifts of these new signals were distinguishable from those of **3a** and the vinylstannane hydrolysis products **6a** and **7a** (156.1, 151.2, 127.7, and 126.1 ppm). To confirm that the signals appearing in solutions of **1** or **2** and **3a** were those of stannyl cuprate adducts **4a** and **5a**, we independently prepared a related vinylcuprate by lithiation/cupration of (*E*)-1-iodo-1-nonene[4]. The ^{13}C NMR spectrum of this species exhibited signals at 132.3 and 125.6 ppm, which are in the same region as those above attributed to vinylcuprates **4a** and **5a**.

Corroborating evidence for the formation of **4** and **5** was gained by monitoring the reaction of [1-^{2}H]-1-decyne (**3b**) by ^{2}H NMR spectroscopy. The onset of addition occurred only above –30 °C and was evidenced by the disappearance of the sharp alkynyl ^{2}H signal at 2.43 ppm with simultaneous formation of a very broad signal (quadrupolar coupling due to copper) centered at 6.3 ppm attributed to **4b** and **5b**. Hydrolysis of this solution with methanol at 0 °C resulted in the disappearance of the broad downfield signal and formation of two overlapping peaks (deuterium is itself a quadrupolar nucleus) at 5.96 and 5.77 ppm, attributed to **6b** and **7b**, respectively.

While **6** and **7** were formed immediately upon quenching reactions of **1** or **2** and **3** with methanol above –30 °C, no products were detected when methanol was added to such solutions maintained between –78 and –35 °C.[5] Solutions in which **4** and **5** had already formed (*T* > –30 °C) could, however, be readily hydrolyzed to **6** and **7** by addition of methanol at temperatures below –30 °C. When the temperatures of solutions containing

1 or 2, 3, and methanol were raised above –30 °C, only product signals due to **6** and **7** (none for **4** and **5**) were observed by ^{13}C and ^{2}H NMR spectroscopy. These observations are in agreement with a two-step process in which vinylcuprates **4** and **5** are formed in a rate-limiting step and are then rapidly hydrolyzed to form **6** and **7**.

To probe the existence of an alkyne–adduct equilibrium, we conducted crossover experiments (eq 2). Thus, to a solution containing an equimolar mixture of stannylcuprate **1** and alkyne **8** (0 °C/1.5 h) was added 1 equiv of alkyne **9** (0 °C/1.5 h). Workup gave a 1:1:1:1 mixture of vinylstannanes **10a**, **10b**, **11a**, and **11b** derived from both **8** and **9**. This result provides compelling evidence for the intermediacy of **12** and **13** which are in equilibrium with starting alkyne. Interestingly, signals due to 1-decyne (**3a**) could not be detected when solutions containing **4a** and **5a** were monitored by ^{13}C NMR spectroscopy between –35 and –78 °C, suggesting a strong thermodynamic preference for the formation of vinylcuprate intermediates over starting materials.

[2]
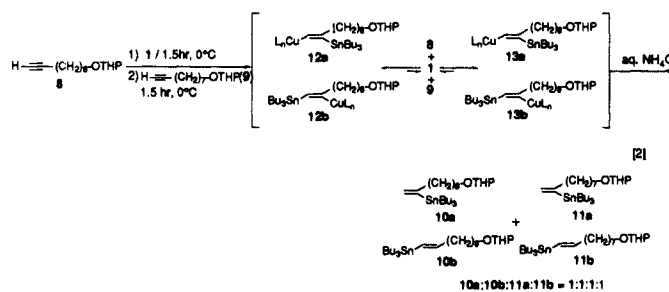
To unequivocally establish that stannylcupration of alkynes is reversible, we subjected distannane **14**[7] to the sequence in eq 3. Thus, reaction of **14** with *n*-BuLi and CuCN·2LiCl would be expected to generate vinylcuprate **12**. Quenching these reactions at –35 °C with methanol gave, as expected, **10a** and **10b**.[8] If equimolar amounts of alkyne **9** were added at 0 °C to solutions containing **12** generated by this alternate route and the resulting solution quenched, nearly equal quantities of **10a**, **10b**, **11a**, and **11b** were obtained in high yield.

[3]
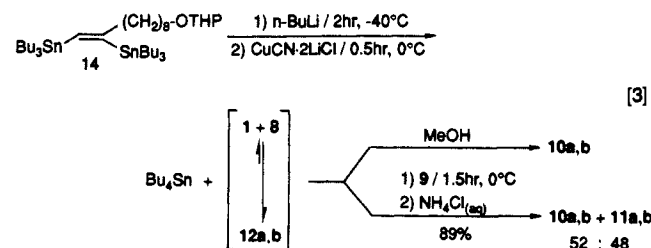
The above raises the possibility that variable regioselectivity in stannycuprations can be obtained through kinetic or thermodynamic capture of the stannyl cuprate intermediates. This question is being currently addressed in our laboratory.

Supplementary Material Available: ^{13}C and ^{2}H NMR spectra of selected solutions at different temperatures (2 pages). Ordering information is given on any current masthead page.

(3) A similar observation was made in the addition of Me$_3$SnCu(CN)Li to [1-^{2}H]-1-octyne. Sharma, S. Ph.D. Thesis, Simon Fraser University, 1989.

(4) Prepared by treatment of (*E*)-1-iodo-1-nonene with 1 equiv of *n*-BuLi (30 min/–30 °C) followed by addition of CuCN·2LiCl in THF.

(5) (Trialkylstannyl)copper reagents **1** and **2** were not hydrolyzed by MeOH between –78 and –35 °C. Parallel observations have been made for related reagents.[1a,d]

(6) It had been established by ^{13}C and ^{2}H NMR spectroscopy that reaction of **1** and **8** was complete under the temperature and time conditions used.

(7) Prepared by reaction of **1** with **8** (–5 °C/1 h) followed by addition of tri-*n*-butylstannyl chloride.

(8) Transmetalation of distannane **14** occurs predominantly at the least hindered 1-stannyl position as was ascertained by quenching the vinyllithium intermediate generated at –78 °C to give an 85:15 mixture of **10a:10b**.