Table II. Kinetic Parameters for Digermene **2** Isomerization

temp, K	K_{eq}	(Z)-**2** → (E)-**2**	(E)-**2** → (Z)-**2**
290.2	0.368	$k_1 = (1.03 \pm 0.02) \times 10^{-5}\ s^{-1}$	$k_{-1} = (2.80 \pm 0.04) \times 10^{-5}\ s^{-1}$
313.3	0.490	$k_1 = (1.90 \pm 0.04) \times 10^{-4}\ s^{-1}$	$k_{-1} = (3.89 \pm 0.07) \times 10^{-4}\ s^{-1}$
		$\Delta H^{\ddagger} = 22.2 \pm 0.3$ kcal mol^{-1}	$\Delta H^{\ddagger} = 20.0 \pm 0.3$ kcal mol^{-1}
		$\Delta S^{\ddagger} = -5 \pm 1$ eu	$\Delta S^{\ddagger} = -10 \pm 1$ eu

Table III. Kinetic Parameters for Isomerizations of Disilenes **7**[a] and **8**

temp, K	K_{eq}	(Z)-**7** → (E)-**7**	(E)-**7** → (Z)-**7**
342.1	1.26	$k_1 = (1.53 \pm 0.03) \times 10^{-5}\ s^{-1}$	$k_{-1} = (1.21 \pm 0.02) \times 10^{-5}\ s^{-1}$
364.0	1.19	$k_1 = (1.67 \pm 0.04) \times 10^{-4}\ s^{-1}$	$k_{-1} = (1.41 \pm 0.02) \times 10^{-4}\ s^{-1}$
		$\Delta H^{\ddagger} = 26.3 \pm 0.5$ kcal mol^{-1}	$\Delta H^{\ddagger} = 27.0 \pm 0.5$ kcal mol^{-1}
		$\Delta S^{\ddagger} = -4.0 \pm 2.0$ eu	$\Delta S^{\ddagger} = -2.4 \pm 2.0$ eu
temp, K	K_{eq}	(Z)-**8** → (E)-**8**	(E)-**8** → (Z)-**8**
337.1	1.29	$k_1 = (1.35 \pm 0.05) \times 10^{-5}\ s^{-1}$	$k_{-1} = (1.05 \pm 0.03) \times 10^{-5}\ s^{-1}$
359.7	1.17	$k_1 = (1.59 \pm 0.03) \times 10^{-4}\ s^{-1}$	$k_{-1} = (1.37 \pm 0.02) \times 10^{-4}\ s^{-1}$
		$\Delta H^{\ddagger} = 25.6 \pm 0.8$ kcal mol^{-1}	$\Delta H^{\ddagger} = 26.7 \pm 0.8$ kcal mol^{-1}
		$\Delta S^{\ddagger} = -5.0 \pm 2.5$ eu	$\Delta S^{\ddagger} = -2.4 \pm 2.5$ eu

[a] The Z assignment to the isolated **7** remains tentative.

Crystallographic Analysis of (Z)-2.[6] The structure of (Z)-**2** has a crystallographic 2-fold axis bisecting the Ge=Ge bond, and pertinent data are summarized in Figure 1 and Table I. The sum of the C–Ge–C and the two C–Ge–Ge′ angles is 345.5°, and there is a sizable pyramidal distortion at the germaniums, reflected in the large fold angle (36°) at these atoms. The Ge=Ge bond length is 2.301 (1) Å. These values are in contrast with those observed for **1**, where the Ge=Ge bond length is noticeably shorter and the fold angle is as small as 12°. The effectively large ligands in (Z)-**2** force the Ge=Ge bond to elongate to the range of distance where mixing of the homo π (b_u) orbital and the σ^* orbital becomes important with increasing fold angle and as a result (Z)-**2** favors a trans-bent conformation.[1] It is interesting to note that the geometries of (Z)-**2** and Lappert's digermene **3**[1g,8,9] are strikingly similar and happen to be in good agreement with the theoretical values (a fold angle of 30–40° and a bond length of 2.27–2.33 Å).[1] Further discussion on the electronic and steric effects of the ligands in **1**–**3** is deferred until more experimental data are accumulated.

$Z \rightleftarrows E$ Isomerization of 2 and Analogous Disilene Derivatives 7 and 8. As noted above, (Z)-**2** in solution is equilibrated with (E)-**2**: the [E]/[Z] values (K_{eq}) in C_6D_6 are 0.490 at 40.1 °C and 0.368 at 17.0 °C. The rates for the $Z \rightleftarrows E$ interconversion were measured in a standard fashion using ^{1}H NMR (500 MHz) spectroscopy, and the kinetic parameters pertinent to these first-order processes are summarized in Table II.[6,10] The rates were unaffected in the presence of 2,3-dimethyl-1,3-butadiene (**5**), an efficient germylene trapping agent. A mixture of **2** and excess **5** did not form, even after a prolonged time at 40 °C, the trapped product **6**, which was obtained upon irradiation of the mixture. Within the limits of its validity, this experiment precludes the possibility that the isomerization proceeds through a thermal dissociation–recombination pathway involving a reactive germylene species and supports the straightforward mechanism of rotation around the Ge,Ge bond axis.

For comparison, kinetic parameters were secured for the isomerization of two newly synthesized disilene derivatives with ligands shown in **7** and **8**, as summarized in Table III.[6,11] It is noted that the enthalpy of activation of the Ge=Ge bond isomerization is somewhat (4–7 kcal/mol) lower than that of the silicon isomerization. Most recent calculations arrive at an estimate of about 25 kcal/mol for the bond categories of both parent disilene and digermene.[1a] Considering the sizable ligands in the derivatives used in the experiments, one concludes that theory and experiment are in good agreement.[12]

Supplementary Material Available: The definitions of fold and twist angles, selected experiments, and listings of physical properties of new dimetallenes and additional information on the X-ray crystal analysis of (Z)-**2** (31 pages). Ordering information is given on any current masthead page.

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(8) (a) Hitchcock, P. B.; Lappert, M. F.; Miles, S. J.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1984**, 480. (b) Fjeldberg, T.; Haaland, A.; Schilling, E. R.; Lappert, M. F.; Thorne, A. J. *J. Chem. Soc., Dalton Trans.* **1986**, 1551.

(9) Compound **3** exists as a digermene only in crystalline form and dissociates into the corresponding germylene (**3a**) in solution, an observation that distinguishes **3** from **2** and also **1** (see text). In view of the structural similarity of **3** and **2**, the small bond dissociation energy associated with **3** appears to be due largely to the unique stabilization of **3a** with the $CH(SiMe_3)_2$ group (β effect) and is not closely related to the conformation of **3**.

(10) No 1,2-diaryl rearrangement was detected during the course of these $Z \rightleftarrows E$ isomerization experiments. Cf.: Yokelson, H. B.; Siegel, D. A.; Millevotte, A. J.; Maxka, J.; West, R. *Organometallics* **1990**, *9*, 1005.

(11) The parameters summarized for **8** in Table III are more accurate than those reported earlier (ref 2c).

(12) We thank Dr. R. S. Grev for providing us with a preprint of ref 1a and the National Science Foundation (Grant CHE-870670) and Kao Corporation, Japan, for financial support.

Structural Characterization of the Three Complexes $[HRe(CO)_4]_n$ (n = 2, 3, 4), Including a Rare Example of a Square Arrangement of Metal Atoms

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The two complexes $[Re_2(\mu\text{-}H)_2(CO)_8]$[1] and $[Re_3(\mu\text{-}H)_3(CO)_{12}]$[2] have been described as organometallic analogues of the $(CH_2)_n$ (n = 2, 3) organic molecules ethylene and cyclopropane.[1] We have now synthesized the organometallic analogue of cyclobutane and we present here the X-ray single-crystal structures of the three members of the family $[HRe(CO)_4]_n$ (n = 2, 3, and 4, compounds **1**, **2**, and **3**, respectively).[3]

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(1) Bennet, M. J.; Graham, W. A. G.; Hoyano, J. K.; Hutcheon, W. L. *J. Am. Chem. Soc.* **1972**, *94*, 6232.

(2) Huggins, D. K.; Fellmann, W.; Smith, J. M.; Kaesz, H. D. *J. Am. Chem. Soc.* **1964**, *86*, 4841.

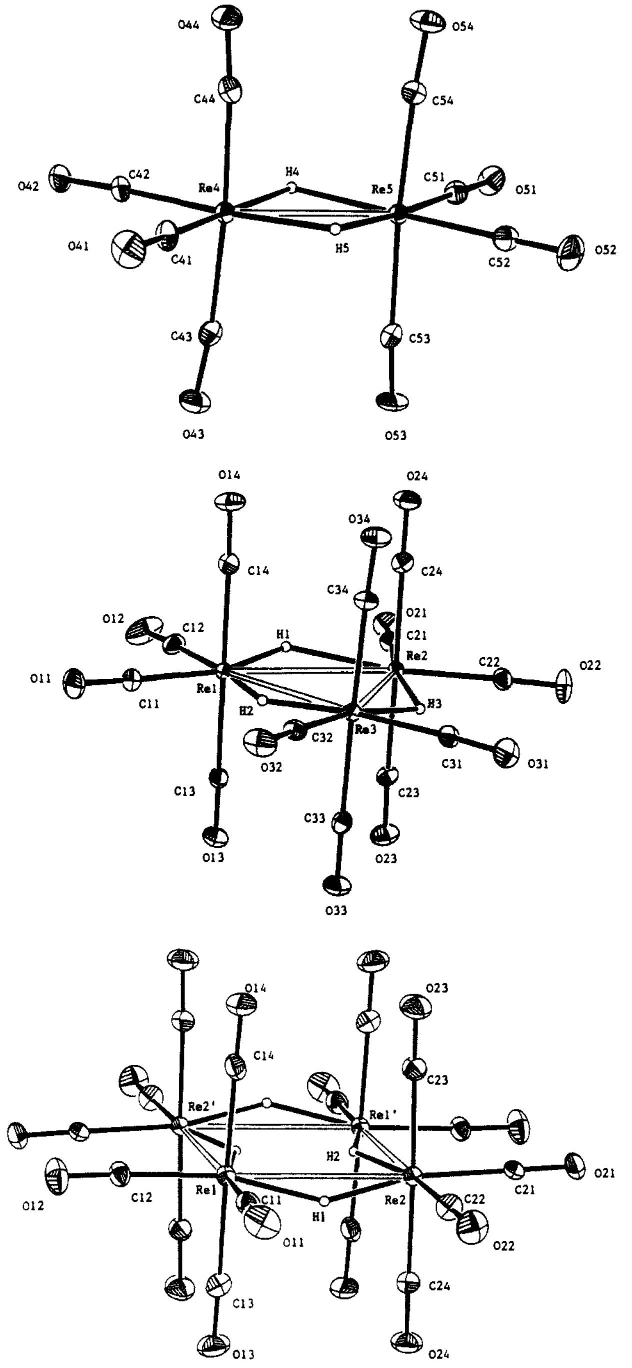

Figure 1. ORTEP drawings of compounds **1** (a, top), **2** (b, middle), and **3** (c, bottom) with labeling scheme. Thermal ellipsoids are drawn at 30% probability.

Scheme I

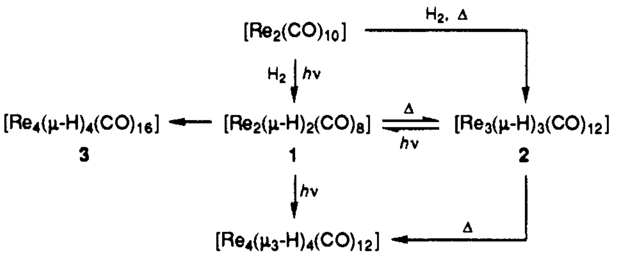

Table I. Relevant Bond Distances and Angles within Compounds **1**, **2**, and **3**[a]

	$n = 2$	$n = 3$	$n = 4$
Re–Re, Å	2.876	3.241 (2)	3.439 (24)
Re–C_{eq}, Å	1.928 (6)	1.931 (5)	1.930 (6)
Re–C_{ax}, Å	1.994 (6)	1.996 (3)	1.996 (6)
C_{eq}–Re–C_{eq}, deg	90.5 (1.6)	92.4 (9)	89.5 (1.2)

[a] Typical esd's on individual values are Re–Re 0.001 Å, Re–C 0.01 Å, and C–Re–C 0.04°. The numbers in parentheses are the standard deviations of the mean ($\bar{x}$), defined as $\sigma_x = [\sum(x_1 - \bar{x})^2/(n - 1)]^{1/2}$.

Compound **1** is stable toward irradiation at wavelengths higher than 300 nm.[5] However, we found that, when irradiated through a quartz vessel in *n*-heptane, compound **1** reacts in a few minutes, giving mainly the unsaturated tetrahedral cluster $[Re_4(\mu_3\text{-}H)_4(CO)_{12}]$, previously obtained by pyrolysis of compound **2**.[6] Furthermore, upon being refluxed in *n*-hexane, **1** gave **2** in good yields, in a reaction that is the thermal reverse of the photochemical **2** ⇒ **1** transformation (Scheme I).[5c] Finally, we observed that **1** slowly decomposes in THF solution, even at room temperature, in the dark, giving mainly **2** and the new species $[Re_4(\mu\text{-}H)_4(CO)_{16}]$ (**3**).[7]

Several crystals of $[Re_4(\mu\text{-}H)_4(CO)_{16}]$,[8] and a small amount of a new phase, shown by X-ray analysis to be the product of cocrystallization of **1** and **2** in a 1:1 ratio,[8] were obtained (beside the previously known crystalline phases of **1** and **2**) while we attempted to grow crystals of **1**.

A selection of the bonding parameters of compounds **1–3** is reported in Table I. $[Re_2(\mu\text{-}H)_2(CO)_8]$ (32 CVEs, Figure 1a) is a dimeric species of D_{2h} idealized symmetry, with the Re–Re bond bridged by two hydrogen atoms. $[Re_3(\mu\text{-}H)_3(CO)_{12}]$ (48 CVEs, Figure 1b) is, as originally proposed by Kaesz,[2] a triangular cluster of D_{3h} idealized symmetry, isostructural with $[Mn_3(\mu\text{-}H)_3(CO)_{12}]$.[9] $[Re_4(\mu\text{-}H)_4(CO)_{16}]$ (64 CVEs, Figure 1c) is a rare example of a square metal cluster with all the Re–Re edges bridged by hydrogen atoms. The molecule lies on a crystallographic inversion center and therefore the four metal atoms are strictly planar; neglecting the hydrides (vide infra), the overall idealized symmetry is D_{4h}. Tetranuclear rhenium clusters of general formula $[Re_4H_x(CO)_y]^{n-}$ are well-known to adopt a wide variety of metal core topologies and different electron counts (ranging from 56 to 64 CVEs);[10] in particular, $[Re_4(\mu\text{-}H)_4(CO)_{16}]$ is isoelectronic

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(3) Although $[Re_3(\mu\text{-}H)_3(CO)_{12}]$ was the first reported hydridocarbonyl cluster of rhenium,[2] it has never been crystallographically characterized, owing to the difficulty of growing crystals of suitable quality.[4] The structure of $[Re_2(\mu\text{-}H)_2(CO)_8]$ has been already described,[1] but due to severe crystal decomposition under diffraction conditions, was poorly defined.

(4) Wei, C.; Garlaschelli, L.; Bau, R.; Koetzle, T. F. *J. Organomet. Chem.* **1981**, *213*, 63.

(5) (a) Byers, B. H.; Brown, T. L. *J. Am. Chem. Soc.* **1975**, *97*, 3260. (b) Andrews, M. A.; Kirtley, S. W.; Kaesz, H. D. *Inorg. Chem.* **1977**, *16*, 1556. (c) Epstein, R. A.; Gaffney, T. R.; Geoffry, G. L.; Gladfelter, W. L.; Henderson, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 3847.

(6) Saillant, R.; Barcelo, G.; Kaesz, H. *J. Am. Chem. Soc.* **1970**, *92*, 5739.

(7) IR (ν_{CO}, THF) 2103 m, 2037 vs, 2015 s, 1970 br m; ^1H NMR ($CDCl_3$) δ −18.1. A white precipitate formed in the reaction, which after several washings with THF (removing mainly **3**) gave a very insoluble residue whose IR and elemental analysis suggest a $[HRe(CO)_4]_n$ formula: IR (Nujol) 2099 s, 2031 vs, 1991 ms, 1962 sh, 1952 vs, 1935 sh. Anal. Calcd for C_4HO_4Re: C, 16.0; H, 0.33. Found: C, 16.4; H, 0.51. Further investigation is in progress.

(8) Compound **3**: $C_{16}H_4O_{16}Re_4$, M_r = 1197.0 g/mol, monoclinic, a = 14.429 (6) Å, b = 12.773 (4) Å, c = 13.483 (4) Å, β = 95.56 (2)°, V = 2473.2 Å^3, Z = 4, space group $C2/c$, D_{calc} = 3.214 g cm^{-3}, μ(Mo Kα) = 198.6 cm^{-1}, max–min transmission factors 1.00–0.69, 4551 measured reflections ($h,k,\pm l$; $6° \le 2\theta \le 50°$), 1443 observed [$I > 5\sigma(I)$] reflections, R = 0.020, and R_w = 0.025. Compound **1·2**: $C_{20}H_5O_{20}Re_5$, M_r = 1496.2 g/mol, triclinic, a = 8.722 (3) Å, b = 13.546 (3) Å, c = 14.179 (3) Å, α = 81.36 (1)°, β = 74.35 (1)° and γ = 81.38 (1)°, V = 1584.3 Å^3, Z = 2, space group $P1$, D_{calc} = 3.136 g cm^{-3}, μ(Mo Kα) = 193.7 cm^{-1}, max–min transmission factors 1.00–0.47, 5547 measured reflections ($h,k,\pm l$); $6° \le 2\theta \le 50°$), 4437 observed [$I > 3\sigma(I)$] reflections, R = 0.024, and R_w = 0.030. Data were collected at room temperature with graphite monochromatized Mo Kα radiation (λ = 0.71073 Å), on an Enraf-Nonius CAD-4 diffractometer and corrected for Lorentz, polarization, and absorption effects.

(9) Kirtley, S. W.; Olsen, J. P.; Bau, R. *J. Am. Chem. Soc.* **1973**, *95*, 4532.

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 $M(\mu\text{-}H)M$ 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 $[Re_4(\mu\text{-}H)_4(CO)_{16}]$. 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 $[Re_3(\mu\text{-}H)_3(CO)_{11}(PPh_3)]$.[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 ^1H 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 $[Re_4(\mu\text{-}H)_4(CO)_{16}]$ 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.

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(10) (a) $[Re_4(\mu\text{-}H)_4(CO)_{12}]$, doubly unsaturated tetrahedron, 56 CVEs: Wilson, R. D.; Bau, R. *J. Am. Chem. Soc.* **1976**, *98*, 4687. (b) $[Re_4(\mu\text{-}H)_3(\mu_3\text{-}H)_2(CO)_{12}]^-$, unsaturated tetrahedron, 58 CVEs: Beringhelli, T.; D'Alfonso, G.; Ciani, G.; Molinari, H. *J. Chem. Soc., Chem. Commun.* **1987**, 486. (c) $[Re_4(\mu\text{-}H)_6(CO)_{12}]^{2-}$, 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) $[Re_4(\mu\text{-}H)_4(CO)_{13}]^{2-}$, 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) $[Re_4(\mu\text{-}H)_5(CO)_{14}]^-$, butterfly, 62 CVEs: Beringhelli, T.; Ciani, G.; D'Alfonso, G., De Maldè, V.; Sironi, A.; Freni, M. *J. Chem. Soc., Dalton Trans.* **1986**, 1051. (g) $[Re_4H(\mu\text{-}H)_3(CO)_{15}]^{2-}$, spiked triangle, 64 CVEs: Ciani, G.; Albano, V. G.; Immirzi, A. *J. Organomet. Chem.* **1976**, *121*, 237. (h) $[Re_4(\mu_4\text{-}C)(CO)_{15}I]^-$, folded square, 64 CVEs: Beringhelli, T.; Ciani, G.; D'Alfonso, G.; Sironi, A.; Freni, M. *J. Chem. Soc. Chem. Commun.* **1985**, 978.

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(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).

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(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

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