Facile addition of alkynes to (CpCo)3(CO)2. A general method for the synthesis of (CpCo)3(CO)(RCCR') complexes

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Table I. First-Order Rate Constants[a] and Activation Parameters[b] for the Cyclization of 5-Decyn-1-yllithium (1) to (1-Cyclopentylidenepent-1-yl)lithium (2)

temp, °C	10^4k, s^{-1}	$\Delta H^‡$, kcal/mol	$\Delta S^‡$, eu
10.0	1.08 ± 0.01	23.0 ± 0.9	+4.8 ± 3.3
14.6	2.61 ± 0.04		
19.0	3.60 ± 0.07		
28.8	15.9 ± 0.7		

[a] Errors are reported as standard deviations. [b] Errors in the activation parameters are reported as maximum errors; see: Wiberg, K. B. *Physical Organic Chemistry*; Wiley: New York, 1964; pp 377–379.

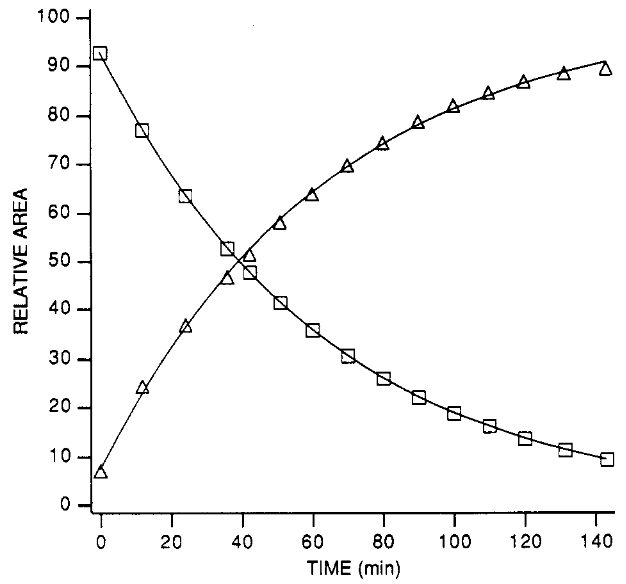
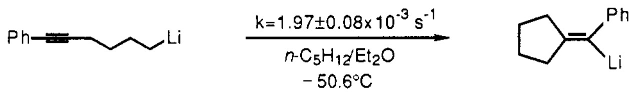


Figure 1. Typical plot of the relative areas of 5-decyn-1-yllithium (□, assayed as 3) and (1-cyclopentylidenepent-1-yl)lithium (△, assayed as 4) as a function of time. Data are from the experiment at 14.6 °C. Solid lines represent the nonlinear least-squares fits of the data.

of 2 (assayed as 4). These data were fit by nonlinear least-squares analysis to the standard exponential form of the first-order rate expression (a typical plot is shown in Figure 1) to give the rate constants reported in Table I. In each instance the rate of disappearance of 1 was identical within experimental error with the rate of appearance of 2. Activation parameters were obtained by application of the Eyring equation: a plot of ln (k/T) versus $1/T$ was linear and gave $\Delta H^‡ = +23.0 \pm 0.9$ kcal/mol and $\Delta S^‡ = +4.8 \pm 3.3$ eu. The corresponding Arrhenius parameters are $E_a = 23.6 \pm 0.9$ kcal/mol and ln $A = 32.9 \pm 3.5$.

A less extensive kinetic analysis of the isomerization of (6-phenyl-5-hexyn-1-yl)lithium (5) to the vinyllithium 6 confirmed the qualitative observation[1] that cyclization of the phenyl-substituted acetylene is much more rapid than that of alkyl-substituted analogues. At −50.6 °C, the first-order rate constant for the cyclization of 5 to 6 is $k = (1.97 \pm 0.08) \times 10^{-3}$ s^{-1}. Thus, the isomerization of 5 to 6, which has a half-life of ~6 min a −50.6 °C, is some 10^6 times more rapid than is the cyclization of 1 to 2 at this temperature. The rather dramatic increase in the rate of cyclization on going from an alkyl-substituted 5-hexyn-1-yllithium to a phenyl-substituted substrate is most likely a consequence of a reduction in $\Delta H^‡$ due to stabilization of the incipient vinyllithium product by the phenyl group.



5 6

It is of interest to note that the 5-exo-dig cyclization of 1 to 2 (and presumably other alkyl-substituted 5-hexyn-1-yllithiums) is slower, at temperatures below ca. +40 °C, than is the corresponding 5-exo-trig isomerization of 5-hexen-1-yllithium to (cyclopentylmethyl)lithium (for which $\Delta H^‡ = 11.8 \pm 0.5$ kcal/mol and $\Delta S^‡ = -30 \pm 2$ eu).[10] Indeed, the activation enthalpy for the intramolecular addition of CH_2Li to an alkyl-substituted acetylene ($\Delta H^‡ = 23.0 \pm 0.9$ kcal/mol, Table I) is about twice that for the analogous addition to an olefin. The small and unexpectedly positive $\Delta S^‡$ value for the cyclization of 1 to 2 may be due to a decrease in the state of aggregation[3] on attaining the transition state, and this, in turn, may reflect a lower state of aggregation of the product vinyllithium (2).

Acknowledgment. This work was supported by the Connecticut Department of Higher Education under Grant No. 90-630 and by a generous unrestricted gift from the Humphrey Chemical Co. of North Haven, CT.

Registry No. 1, 126217-30-9; 2, 126217-31-0; 3, 1942-46-7; 4, 53366-55-5; 5, 126217-32-1; 6, 126217-33-2; 1-iodo-5-decyne, 42049-41-2.

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(10) Bailey, W. F.; Patricia, J. J.; DelGobbo, V. C.; Jarret, R. M.; Okarma, P. J. *J. Org. Chem.* 1985, *50*, 1999.

Facile Addition of Alkynes to $(CpCo)_3(CO)_2$. General Method for the Synthesis of $(CpCo)_3(CO)(RCCR')$ Complexes

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Summary: Incorporation of alkynes into the framework of $(CpCo)_3(CO)_2$ occurs at room temperature to produce alkyne–carbonyl complexes of the form $(CpCo)_3(CO)(RCCR')$. The structure of the 3-hexyne adduct is described as well as preliminary observations on the dynamic properties of these complexes.

A wide variety of transition-metal complexes containing alkyne ligands now exists in which this ligand interacts with one or more metal atoms.[1] Although many examples of cluster complexes of the form $M_3(CO)_n$(alkyne) have been described, relatively few are known for the corresponding Cp_3M_3 (Cp = η^5-cyclopentadiene) systems. We recently described the synthesis and properties of a new series of 46-electron Fischer–Palm type trinuclear clusters $(Cp'M)_3(CO)_2$ that readily react with two-electron ligands.[2] Here we describe a convenient, general method for the introduction of a wide variety of alkynes, diynes, and functionalized alkynes into the trinuclear framework of $(CpCo)_3(CO)_2$, 1. Two isomeric adducts (referred to as static and dynamic isomers) may be obtained depending

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(1) Sappa, E.; Tirpicchio, A.; Braunstein, P. *Chem. Rev.* 1983, *83*, 203–239, and references therein.

(2) (a) Barnes, C. E.; Dial, M. R. *Organometallics* 1988, *7*, 782–784. (b) Herrmann, W. A.; Barnes, C. E.; Zahn, T.; Ziegler, M. L. *Organometallics* 1985, *4*, 172–180. (c) Barnes, C. E.; Orvis, J. A.; Staley, D. L.; Rheingold, A. L.; Johnson, D. C. *J. Am. Chem. Soc.* 1989, *111*, 4992–4994. (d) Barnes, C. E.; Dial, M. R.; Orvis, J. A.; Staley, D. L.; Rheingold, A. L. *Organometallics*, in press.

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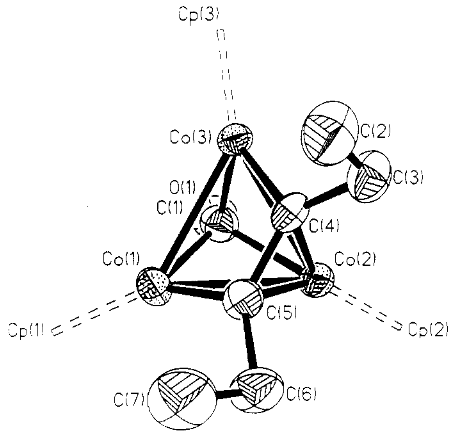
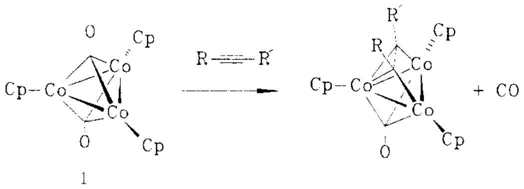


Figure 1. ORTEP view of **4** (Cp rings have been removed for clarity).

Scheme I



1

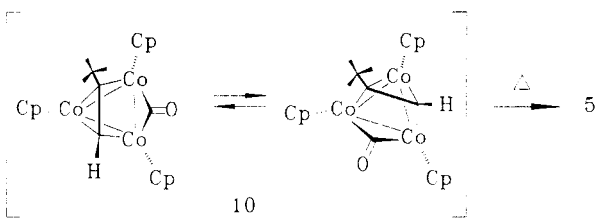
2 R = R' = H
3 R = R' = Me
4 R = R' = Et
5 R = C(CH$_3$)$_3$ R' = H
6 R = Ph R' = H
7 R = R' = Ph
8 R = R' = CH$_2$OH
9 R = R' = CO$_2$CH$_3$

on the size and nature of the substituents on the alkyne. The conversion of the static to the dynamic isomer has been studied in the case of the *tert*-butylacetylene adduct. The solid-state structure of the 3-hexyne complex is described.

As shown in Scheme I, reaction of **1** with different alkynes gives rise to the monoalkyne monocarbonyl complexes, **2–9**.[3] In every case, one carbonyl ligand of **1** is replaced by the alkyne, which formally donates four electrons to the valence shell of the cluster. Good yields are obtained with sterically hindered alkynes (**5–7**) as well as with alkynes containing functional groups (**8**, **9**).

The spectroscopic properties[4] of **2–9** are consistent with a general structure type that has the alkyne ligand on one

Scheme II

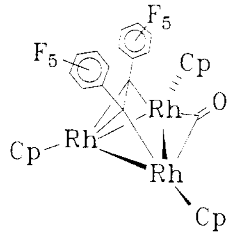


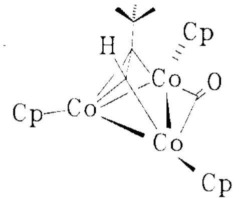
10

side of the tricobalt plane and a triply bridging carbonyl ligand (ν_{CO} = 1699–1692 cm^{-1}, hexane) on the other. In solution, the equivalence of the Cp rings (^{1}H, ^{13}C NMR) in all examples of these complexes is consistent with free rotation of the alkyne ligand around a pseudo-3-fold rotation axis at room temperature. A variable-temperature NMR study of the *tert*-butylacetylene adduct **5** showed no signs of coalescence broadening at −100 °C, indicating the barriers to alkyne rotation are low in this case.[5]

The structure of the 3-hexyne adduct **4**[6] has been determined. Figure 1 shows an ORTEP view of the complex with the Cp rings removed for clarity. The alkyne is oriented parallel to one Co–Co edge and offset toward the unique cobalt atom. The Co–C$_{alkyne}$ distances may be divided into two groups: two long distances to the unique cobalt atom (C$_4$–Co$_2$ 1.986 (3) Å, C$_5$–Co$_2$ 1.995 (3) Å) and two short distances (C$_4$–Co$_3$ 1.917 (4) Å, C$_5$–Co$_1$ 1.903 (4) Å). The Co$_1$–Co$_3$ edge (2.480 (1) Å) parallel to the alkyne bond is somewhat longer than the other Co–Co separations, (Co$_1$–Co$_2$ 2.440 (1) Å; Co$_2$–Co$_3$ 2.428 (1) Å). The alkyne group causes the Cp ligands move below the plane of the metal atoms.[7] The separation of the two alkyne carbons (1.370 (5) Å) and bending of the ethyl substituents away from the alkyne bond axis (average 127.0 ± 0.5°) are consistent with a reduction of the bond order between the two carbons to two.[8]

A second isomer, **10**, is formed in the case of the *tert*-butylacetylene adduct. The proton and carbon spectra[9] for **10** are consistent with a static structure in which the





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alkyne is positioned across two of the Co–Co edges. The IR band (1803 cm^{-1} (CH$_2$Cl$_2$)) for the carbonyl ligand in-

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[3] Isolated yields (after chromatography) of 40–90% are typical for these reactions, based on **1**.

[4] Spectroscopic and analysis data: **2**: ^{1}H NMR (200 MHz, C$_6$D$_6$ 7.15 ppm) δ 4.515 (s, 15 H), 10.235 (s, 2 H); ^{13}C{^{1}H} NMR (C$_6$D$_6$ 128 ppm) δ 84.603 (Cp), 138.092 (H—*C*≡); IR (CH$_2$Cl$_2$): ν_{CO} 1680 cm^{-1}. **3**: ^{1}H NMR 4.464 (s, 15 H), 2.747 (s, 6 H); ^{13}C{^{1}H} δ 85.679 (Cp), 156.36 (*C*≡*C*), 31.07 (*C*H$_3$); IR (CH$_2$Cl$_2$) ν_{CO} 1669 cm^{-1}. Anal. Calcd for C$_{20}$H$_{21}$Co$_3$O: C, 52.89; H, 4.66. Found: C, 52.77; H, 4.49. **4**: ^{1}H NMR δ 4.512 (s 15 H), 2.87 (q, 7.35 Hz, 4 H), 1.42 (t, 7.35 Hz, 6 H); ^{13}C{^{1}H} (C$_6$D$_6$) δ 164.5 (*C*≡), 85.55 (Cp *C*), 38.03 (*C*H$_2$), 16.06 (*C*H$_3$); IR (CH$_2$Cl$_2$) ν_{CO} 1671 cm^{-1}. **5**: ^{1}H NMR δ 10.303 (s, 1 H), 4.566 (s, 15 H), 1.491 (s, 9 H); ^{13}C{^{1}H} (CD$_2$Cl$_2$ 53.8) δ 281.5 (br, *C*O) 174.9 (*C*≡), 132.8 (H*C*≡), 83.8 Cp, 42.2 (*C*(CH$_3$)$_3$), 31.7 (C(*C*H$_3$)$_3$); IR (CH$_2$Cl$_2$) ν_{CO} 1672 cm^{-1}. Anal. Calcd for C$_{22}$H$_{25}$Co$_3$O: C, 54.90; H, 5.02. Found: C, 54.57; H, 5.02. **6**: ^{1}H NMR δ 10.383 (s, 1 H), 7.2–7.6 (m, 5 H), 4.470 (s, 15 H); ^{13}C{^{1}H} NMR δ 154.346, 151.638 (quaternary phenyl C and *C*≡), 132.966 (H*C*≡), 85.72 (Cp *C*); IR (CH$_2$Cl$_2$) ν_{CO} 1680 cm^{-1}. **7**: ^{1}H NMR (400 MHz, acetone-*d*$_6$ δ 2.04) δ 7.596 (d of t, 6.8 and 1.6 Hz, H$_o$), 7.270 (t of t, 7.2 and 1.0 Hz, H$_p$), 7.130 (t of t, 7.2 and 1.1 Hz, H$_m$) 4.597 (s, 15 H); ^{13}C{^{1}H} NMR (acetone-*d*$_6$) δ 152.0, 156.1 (quaternary Ph C and *C*≡), 129.5, 128.3, 126.1 (Ph C), 88.0 (Cp); IR (CH$_2$Cl$_2$) ν_{CO} 1682 cm^{-1}. Anal. Calcd for C$_{30}$H$_{25}$Co$_3$O: C, 62.31; H, 4.36. Found: C, 62.10; H, 4.24. **8**: ^{1}H NMR (acetone-*d*$_6$) δ 4.670 (s, 15 H), 5.10 (s, 2 H), 5.01 (s, 4 H); ^{13}C{^{1}H} NMR (acetone-*d*$_6$) δ 160.16 (*C*≡C), 85.81 (Cp), 73.30 (*C*H$_2$); IR (CH$_2$Cl$_2$) ν_{CO} 1684, ν_{OH} 3593 cm^{-1}. **9**: ^{1}H NMR δ 4.669 (s, 15 H), 3.641 (s, 6 H); ^{13}C{^{1}H} (CD$_2$Cl$_2$) δ 277.701 (*C*O), 175.393 (*C*≡*C*), 140.577 (*C*$_{ester}$O), 86.613 (Cp), 52.201 (*C*H$_3$); IR ($\nu_{CO} + \nu_{CO_{ester}}$) 1694 (CH$_2Cl_2$), 1706 (m), 1691 (s), 1673 (m) (KBr) cm^{-1}.

[5] Similar behavior has been described for other trinuclear systems; cf.: (a) Eaton, B.; O'Connor, J. M.; Vollhardt, K. P. C. *Organometallics* **1986**, *5*, 394–397. (b) Yamamoto, T.; Garber, A. R.; Bodner, G. M.; Todd, L. J.; Rausch, M. D.; Gardner, S. A. *J. Organomet. Chem.* **1973**, *56*, C23–C26. (c) Todd, L. J.; Wilkinson, J. R.; Rausch, M. D.; Gardner, S. A.; Dickson, R. S. *J. Organomet. Chem.* **1975**, *101*, 133–138.

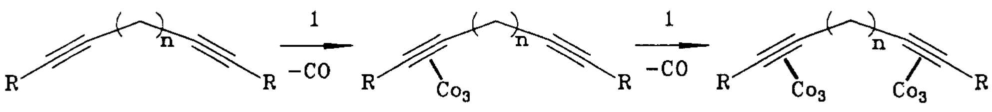
[6] Black rhombohedral crystals from hexane, monoclinic, $P2_1/n$; a = 9.0503 (13) Å, b = 14.423 (3) Å, c = 15.177 (2) Å, β = 107.000 (12)°; Z = 4; R = 0.0371, R_w = 0.0379. A complete description of the structure and refinement details is given in the supplementary material (see the paragraph at the end of the paper).

[7] Angles between the Cp$_{centroid}$–Co vectors and the plane of the metal atoms in **4**: Co$_1$, 168°; Co$_2$ 165°; Co$_3$ 167°.

[8] (a) Dodge, R. P.; Schomaker, V. *J. Organomet. Chem.* **1965**, *3*, 274–284. (b) Ferraris, G.; Gervasio, G. *J. Chem. Soc., Dalton Trans.* **1973**, 1933–1936. (c) Tachikawa, J. R.; Shapley, J. R.; Pierpont, C. G. *J. Am. Chem. Soc.* **1975**, *97*, 7172–7174.

[9] Spectroscopic data for **10**: ^{1}H NMR (C$_6$D$_6$ 200 MHz) δ 9.993 (s, 1 H), 4.763 (s, 5 H), 4.634 (s, 5 H), 4.520 (s, 5 H), 1.357 (s, 9 H); ^{13}C{^{1}H} NMR δ 232.87 (*C*O, br), 195.08 (*C*≡), 164.88 (H–*C*≡), {92.06, 87.86, 80.41} (Cp, *C*), 36.09 (*C*(CH$_3$)$_3$), 29.09 (C(*C*H$_3$)$_3$); IR (CH$_2$Cl$_2$) 1803 cm^{-1}.

Scheme III



Co_3 = $(CpCo)_3(CO)$

11 n = 0 R = CH_3
12 n = 0 R = CH_2OH
13 n = 2 R = H
14 n = 6 R = CH_3

15 n = 2 R = H
16 n = 6 R = CH_3

dicates an edge-bridging geometry. Similar spectroscopic characteristics have been reported for a trirhodium bis(pentafluorophenyl)acetylene complex, $(CpRh)_3(CO)(C_6F_5C_2C_6F_5)$,[10] in which both the acetylene and the edge bridging carbonyl ligand are on the same side of the trirhodium plane. We assume that **10** has the same overall structure.[11]

Heating **10** to 100 °C in toluene causes clean, irreversible transformation to **5**.[12] As this isomerization takes place, an NMR study reveals that between 70 and 100 °C the two downfield Cp signals of **10** coalesce to form a single peak.[13] The energy barrier for this process is estimated to be 17.5 kcal/mol.[14] The isomerization of **10** to **5** follows first-order kinetics in toluene-d_8 ($t_{1/2}$ = 56 min, 80 °C). NOE enhancements are observed only for the downfield Cp signals of **10** at 4.76 and 4.63 ppm when the *tert*-butyl signal was irradiated.[15] Irradiation of each of the Cp signals at 40 and 60 °C gave rise to magnetization transfer only between the signals at 4.76 and 4.63 ppm.

These data are consistent with the following two processes (Scheme II). The first involves a "windshield wiper" movement of the unsubstituted end of the alkyne between two Co–Co edges of the Co_3 triangle with synchronous movement of the carbonyl ligand between the same two edges.[16] This process equilibrates the two enantiomers of **10** and accounts for the coalescence behavior observed in the NMR spectrum. The second process is irreversible and involves the movement of the carbonyl ligand from a Co–Co edge to a triply bridging coordination geometry on the Co_3 face opposite the alkyne ligand. The temperature at which the isomerization takes place is far above that at which these isomers are initially formed from **1**. Preliminary experiments indicate that neither added CO nor excess alkyne catalyze the isomerization of **10** to **5**.

Clean, sequential mono- and diaddition of **1** to diynes has also been observed as illustrated in Scheme III.

In all cases the first addition of **1** to a diyne yields the fluxional adduct analogous to **5**. The second addition yields either the fluxional or the static adduct (e.g., **10**) depending on the steric bulk and proximity of the substituents on the triple bond.[17] The examples above illustrate the scope of this reaction with respect to the alkyne substrate. Similar products are obtained when mixed metal analogues to **1** are exposed to alkynes.[2a] We are currently investigating schemes for the remote functionalization and linking of these and other "$(CpM)_3$"–alkyne adducts to produce charge-transfer species and organometallic polymers.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Johnson Matthey Co. for their generous loan of precious-metal starting materials.

Registry No. **1**, 121232-36-8; **2**, 126217-64-9; **3**, 126217-65-0; **4**, 126217-66-1; **5**, 126217-67-2; **6**, 126217-68-3; **7**, 126217-69-4; **8**, 126217-70-7; **9**, 126217-71-8; **10**, 126217-72-9; 11, 126217-73-0; **12**, 126217-74-1; **13**, 126217-75-2; **14**, 126217-76-3; **15a**, 126217-77-4; **15b**, 126217-79-6; **16**, 126217-78-5; HC≡CH, 74-86-2; MeC≡CMe, 503-17-3; EtC≡CEt, 928-49-4; $(CH_3)_3CC{\equiv}CH$, 917-92-0; PhC≡CH, 536-74-3; PhC≡CPh, 501-65-5; $HOCH_2C{\equiv}CCH_2OH$, 110-65-6; $CH_3CO_2C{\equiv}CCO_2CH_3$, 762-42-5; $CH_3C{\equiv}CC{\equiv}CCH_3$, 2809-69-0; $HOCH_2C{\equiv}CC{\equiv}CCH_2OH$, 3031-68-3; $HC{\equiv}C(CH_2)_2C{\equiv}CH$, 628-16-0; $CH_3C{\equiv}C(CH_2)_6C{\equiv}CCH_3$, 31699-38-4.

Supplementary Material Available: Tables of crystal data and summary of data collection and refinement, ORTEP illustration showing numbering scheme for all atoms, and tables of fractional coordinates, thermal parameters, anisotropic thermal parameters, interatomic distances, and interatomic angles for **4** and spectroscopic data for complexes **11**–**16** (9 pages); a listing of structure factors for **4** (9 pages). Ordering information is given on any current masthead page.

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(10) Trinh-Toan, P. W.; Broach, S. A.; Gardner, M. R.; Rausch, M. R.; Dahl, L. F. *Inorg. Chem.* **1977**, *16*, 279–289.

(11) The position of the carbonyl ligand relative to the unsymmetrical alkyne in **10** is as yet undetermined. Assuming the carbonyl and acetylene ligands are on the same side of the tricobalt plane, the carbonyl ligand should bridge the edge opposite the alkyne ligand as observed in the rhodium complex.

(12) One other system has been described in which the static and dynamic isomers of this type of trinuclear complex may be equilibrated: Dickson, R. S.; Mok, C.; Pain, G. *J. Organomet. Chem.* **1979**, *166*, 385–402.

(13) The coalescence phenomenon is completely reversible and distinct from the isomerization of **10** to **5**.

(14) From line width and separation of signals for the static, low-temperature limit and the coalescence temperature.

(15) Corresponding NOE effects were observed for the Cp signal at 4.52 ppm when the acetylene proton signal was irradiated.

(16) The exact mechanistic sequence for the this process and the irreversible isomerization of **10** to **5** remain unclear. Investigations are in progress to define more clearly this behavior.

(17) Monoaddition of **1** to 1,5-hexadiyne gives rise to the fluxional adduct. Diaddition gives rise to mixtures of both the fluxional–fluxional and fluxional–static adducts which have been isolated, separated, and characterized. Spectroscopic data (IR, ^1H, ^{13}C NMR) for complexes **11**–**16** are provided in the supplementary material.

Carbon–Carbon Coupling between Olefinic C Atoms on a Cluster as a Lewis Acid–Base Reaction

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Summary: The CH_2 group of the nonpolar cluster compound $FeCo_2(CO)_9(\mu_3\text{-}\eta^2\text{-}C{=}CH_2)$ as a Lewis acid has been attached to the methylene group of the neutral phosphorus ylides $Ph_3P{=}CHR$ (R = H, $SiMe_3$, C(O)Ph, COOEt) as a Lewis base. This is the first case of a Lewis acid–base combination of two uncharged methylene units resulting in an isolable primary product.

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