electron transfer from naphthalene in hexadecane to $Co(NH_3)_6^{3+}$ in water.[10,11]

Conclusion. In suitable cases the phase-transfer photolysis which features the separation of reactants and products may be developed to a useful synthetic procedure in organometallic chemistry. Under appropriate conditions inner-filter effects and secondary photolysis which frequently hamper the photolysis in homogeneous solution can be avoided.

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Linear Trimerization of Phenylethyne: Homogeneous Catalysis with *triangulo*-$Co_3(\mu_3\text{-}H)(\mu_2\text{-}CO)_3(PMe_3)_6$

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Summary: Phenylacetylene at 100 °C in the presence of catalytic amounts of the triangulo cluster $Co_3(\mu_3\text{-}H)(\mu_2\text{-}CO)_3(PMe_3)_6$ is transformed into a linear trimer with high regioselectivity and stereoselectivity. Crystals of the new dienyne Ph(PhC≡C)C=CHCH=CHPh in an X-ray structure study are shown to contain molecules in the most stable conformation as expected from MNDO calculations.

Homogeneous catalysis with transition-metal cluster molecules is a promising route to new forms of catalytic activity. While there is no convincing argument against the suspicion that undetected mononuclear intermediates may act as effective catalysts,[1] cluster catalysis continues to supply efficient syntheses that do not succeed without clusters.[2]

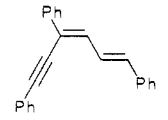
Investigating trimethylphosphine complexes of low-valent cobalt and nickel, we found an easy access to molecular clusters of the triangulo type.[3] Irradiation of freely soluble mononuclear compounds of Co(0) and Ni(0) in toluene over 3 h at 80 °C resulted in deposition of the sparingly soluble title compound 1 in 45% yield.[4] Under these conditions no nickel is incorporated (e.g. from $Ni(CO)(PMe_3)_3$ as a convenient source of carbonyl ligands).

$$2\,Co(C_2H_4)(PMe_3)_3 + Ni(CO)(PMe_3)_3 \xrightarrow[h\nu]{-C_2H_4,\ -NiL_4} \underset{\mathbf{1}}{Co_3(H)(CO)_3(PMe_3)_6} \quad (1)$$

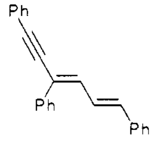
Table I. Calculated Heats of Formation (kcal mol^{-1}) of Isomers 2A and 2B, Based on Atomic Coordinates Found

	heat of formation			
method[a]	2A	2B	Δ	RMS[b]
AM 1	151.54	152.70	−1.16	0.468
PM 3	151.81	155.33	−3.52	0.389
MNDO	144.48	144.62	−0.14	1.022
MNDO[c]	144.36	145.08	−0.72	1.216

[a] Semiempirical (program packages MOPAC, version 5.0). [b] Deviations of calculated and structurally found molecular geometry. [c] Based on models 2A and 2B:

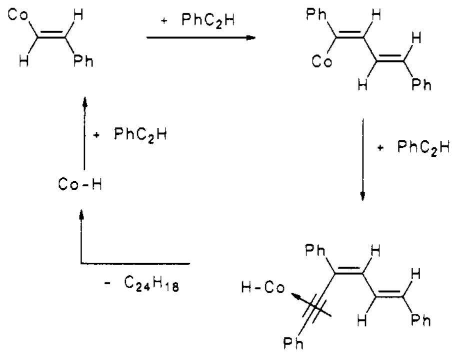


2A



2B

Scheme I. Important Steps in the Linear Trimerization of Phenylethyne[a]



[a] Co stands for a cluster or a mononuclear complex moiety.

Treatment of the D_{3h} cluster 1 (Figure 1) with phenylacetylene for the first time induces a highly selective linear trimerization that does not proceed with mononuclear catalysts, where cyclic oligomers are predominantly formed.[5] As the main product of a typical synthesis[6] (from

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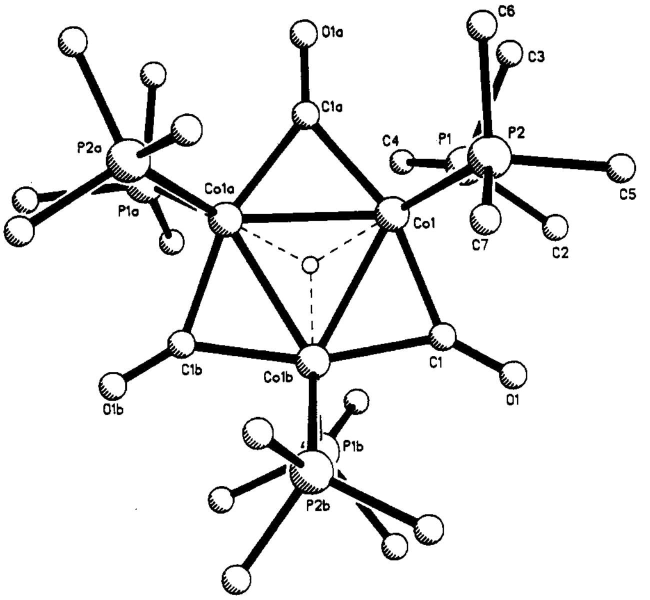

Figure 1. Molecular structure of 1.

C_8H_6 and 1 (500:1) at 100 °C over 3 h, 83% isolated yield) **2A** is separated from a red oil containing all the cobalt, which has not yet been characterized. In a repeated experiment the reaction was carried out to give a homogeneous system that was left overnight at 20 °C. On the next day this was charged with an equal amount of phenylacetylene and trimerization was effected under the same conditions. So far we have not been able to decide whether a tricobalt derivative of 1 with a hydrocarbon ligand or a mononuclear species is the living catalyst.

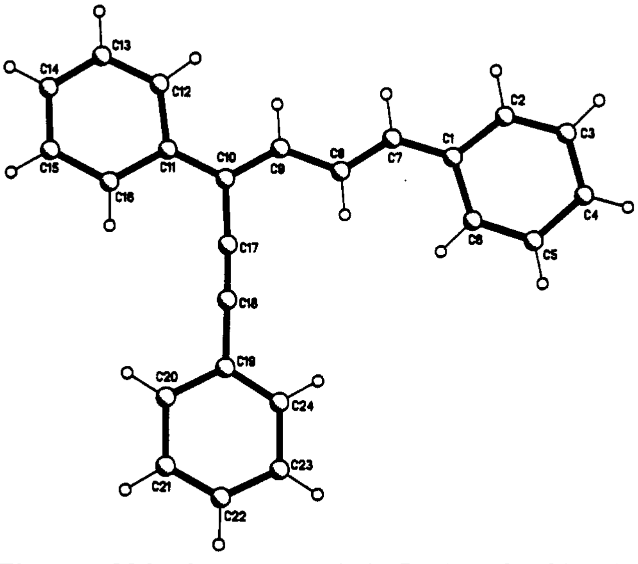

Figure 2. Molecular structure of **2A**. Pertinent bond lengths (Å) and bond angles (deg) are as follows: C1–C7 = 1.370 (22), C7–C8 = 1.313 (24), C8–C9 = 1.405 (29), C9–C10 = 1.363 (28), C10–C11 = 1.415 (30), C10–C17 = 1.431 (27), C17–C18 = 1.186 (24), C18–C19 = 1.448 (22); C1–C7–C8 = 130.1 (16), C7–C8–C9 = 126.3 (18), C8–C9–C10 = 129.3 (17), C9–C10–C17 = 117.2 (20), C10–C17–C18 = 174.2 (27), C17–C18–C19 = 176.5 (25).

Figure 2 shows the configuration of the new dieneyne[7,8] as elucidated by an X-ray crystal structure analysis.[9] The configuration of **2A** observed in the crystal corresponds to what is expected from MNDO calculations (Table I) to be the thermodynamically controlled isomer. Isomer **2B** was not found among the products.

The formation of **2A** can be explained by successive steps of oxidative-addition and formal insertion reactions (Scheme I). End-to-end coupling of two 1-alkynes has also been observed at single metal centers,[10] but to the best of our knowledge a subsequent step of formal addition of a third alkyne to the chain has not been reported.

In the formation of acyclic products migration of a hydride ligand must be a decisive step. Supporting evidence comes from a high-yield reaction of phenylacetylene and 1 in a 1:1 ratio, giving an intermediate that does not display $\nu(C{\equiv}C)$ or $\nu({\equiv}CH)$ absorptions in the infrared spectrum. This compound is under investigation.

Trimerization of acetylenecarboxylic acid ethyl ester is achieved under similar conditions (100 °C, 5 h). The selectivity of this catalytic reaction is only slightly (85–90%) lower but is directed toward the cyclic trimer 1,2,4-tris(ethoxycarbonyl)benzene and is believed to proceed by a different mechanism.

Acknowledgment. Financial support from the Fonds der Chemischen Industrie and from the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

Supplementary Material Available: Tables of positional parameters, bond distances and angles, and isotropic thermal parameters for **2A** (4 pages). Ordering information is given on any current masthead page.

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(6) Procedure: 20 mg (0.028 mmol) of 1 and 6.07 g (59.4 mmol) of phenylacetylene under 1 bar of Ar were heated to 100 °C with vigorous stirring. After 3 h the homogeneous red liquid was brought to 20 °C and 20 mL of 6 M HCl was added. Extraction with ether gave 6 g of an orange-red oil. Chromatography of 600 mg of this oil on Al_2O_3 (neutral, I) with pentane/CH_2Cl_2 (10:1): Small amounts of forerunning byproducts (1,2,4-triphenylbenzene and (*E*)-1,4-diphenylbut-1-en-3-yne) were discarded. Bright orange **2A** was recrystallized from ethanol, yielding 500 mg of yellow needles, mp 106–107 °C dec. Color test for **2A** with concentrated H_2SO_4: A few crystals of **2A** (ca. 5 mg) in 1 mL of toluene are shaken with 0.5 mL of concentrated sulfuric acid. The lower phase displays an intense cherry red.

(7) Analytical characterization of **2A**. Anal. Calcd for $C_{24}H_{18}$ (M_r 306.41): C, 94.08; H, 5.92. Found: C, 94.17; H, 5.70. ^1H NMR (300 MHz, CD_2Cl_2, 25 °C, TMS internal reference): $\delta = 6.9$ (dd, $^3J(HH) = 15.6, 0.8$ Hz, 1 H, CH), 7.2 (dd, $^3J(HH) = 11.1, 0.8$ Hz, 1 H, CH), 7.6 (dd, $^3J(HH) = 11.1, 15.6$ Hz, 1 H, CH), 7.2–7.8 (m, 15 H, C_6H_5). ^{13}C NMR (75.4 MHz, CD_2Cl_2, TMS internal reference): δ 87.22, 98.36 ($-C{\equiv}C-$). UV/vis (CH_2Cl_2; λ_{max}, nm (ϵ)): 278 (22 600), 286 (21 900), 362 (33 600). MS (70 eV): m/z 306 (M^+).

(8) A compound described earlier with formula **2A** has different properties and must have a different structure: (a) Meriwether, L. S.; Colthup, E. C.; Kennerly, G. W.; Reusch, R. N. *J. Org. Chem.* **1961**, *26*, 5155. (b) Booth, G.; Rowe, J. M. *Chem. Ind.* (*London*) **1960**, 661.

(9) Crystal data for **2A**: $C_{24}H_{18}$, M_r 306.4, crystal dimensions 0.31 × 0.32 × 0.55 mm, orthorhombic, space group $Pca2_1$ (No. 29), $a = 12.021$ (2) Å, $b = 16.446$ (3) Å, $c = 8.956$ (2) Å, $V = 1770.6$ Å^3, $Z = 4$, $d_{calcd} = 1.149$ g cm^{-3}, $\mu = 0.06$ mm^{-1}, $F(000) = 648$, $T = 296$ (1) K, Siemens R3m/V diffractometer, $\lambda = 0.71069$ Å, scan mode ω–2θ, 2383 reflections measured $3 \leq 2\theta \leq 55°$, $0 \leq h \leq 11$, $0 \leq k \leq 15$, $0 \leq l \leq 21$, low scattering gave only 595 observed reflections ($F < 4\sigma/F$), 96 refined parameters, direct methods, H atoms in idealized positions with $U_{iso} = 0.08$ Å, isotropic refinement of C atoms, $R = 0.106$, $R_w = 0.081$ ($1/w = \sigma^2(F) + 0.0001F^2$), $S = 2.581$, $(\Delta/\sigma)_{max} = 0.001$, maximum residual electron density 0.60 e Å^{-3}. Scattering factors, structure solution, and refinement were determined by SHELXTL-PLUS (Siemens, 1990). For other details see the supplementary material.

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