Pergamon

Tetrahedron Letters 41 (2000) 4261–4264

TETRAHEDRON
LETTERS

An unusual cobalt-mediated cleavage of a hindered alkyne

Naoto Hayashi, Douglas M. Ho and Robert A. Pascal Jr.*

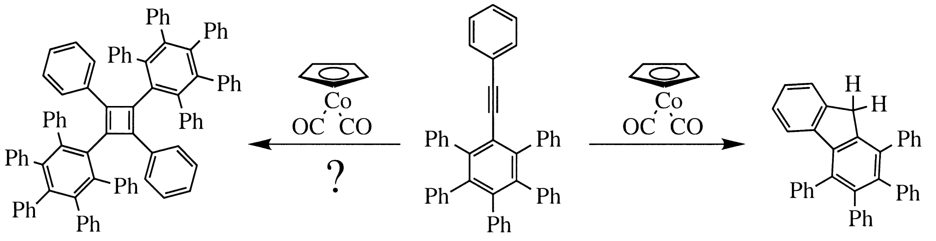
Department of Chemistry, Princeton University, Princeton, New Jersey 08544, USA

Received 29 March 2000; accepted 20 April 2000

Abstract

When 1-(pentaphenylphenyl)-2-phenylacetylene (**1**) is heated with (η^5-cyclopentadienyl)dicarbonylcobalt, 1,2,3,4-tetraphenylfluorene (**3**) and related minor products are formed rather than the expected tetraarylcyclobutadiene. The formation of **3** requires that a seven-carbon fragment (formally a phenylcarbyne) must be lost. Two minor products, however, result from intramolecular cyclization of the alkyne and these two retain all of the carbons from the starting material. © 2000 Elsevier Science Ltd. All rights reserved.

We recently described the synthesis 1,3,5-tris(pentaphenylphenyl)benzene, a crowded molecule in which the central benzene ring is completely shielded from the surrounding solvent by the pentaphenylphenyl groups.[1] This tremendously bulky substituent is easy to prepare, and it should admirably protect even extremely reactive functional groups. In order to test this hypothesis, we attempted to prepare 1,3-bis(pentaphenylphenyl)-2,4-diphenylcyclobutadiene (**2**) by dimerization of the readily available 1-(pentaphenylphenyl)-2-phenylacetylene[2] (**1**). (η^5-Cyclopentadienyl)-dicarbonylcobalt has been used for the conversion of other hindered, asymmetric alkynes, including naphthylphenylacetylene and mesitylphenylacetylene, to the corresponding cyclobutadiene complexes;[3,4] it is readily available, and so it seemed to be the reagent of choice for such a synthesis.



2 **1** **3**

For the dimerization of mesitylphenylacetylene, Rausch et al. heated 2 equivalents of the acetylene with 1 equivalent of $CpCo(CO)_2$ in refluxing xylenes for 72 h.[4] When we attempted

---

* Corresponding author.

0040-4039/00/$ - see front matter © 2000 Elsevier Science Ltd. All rights reserved.

PII: S0040-4039(00)00667-5

similar dimerizations of compound **1** under these conditions, the reaction was sluggish, even when refluxing tetralin was substituted for xylenes. No organometallic products were isolated from these mixtures, and the main organic product found in each case proved to be 1,2,3,4-tetraphenylfluorene (**3**, $C_{37}H_{26}$), which necessitates the loss of a seven-carbon fragment from **1** ($C_{44}H_{30}$). This result was quite unexpected, and so we analyzed the products from one of the large-scale reactions in detail. In this case 10.24 g (18.33 mmol) of **1** were heated with 1.65 g (9.16 mmol) of $CpCo(CO)_2$ in 150 mL xylenes, and most of the starting material was consumed after 144 h at reflux. Three high molecular weight organic products were obtained after repeated silica gel column chromatography: compounds **3** (2.05 g), **4** (80 mg), **5** (70 mg), and mixtures of the three (0.85 g).

The ^1H and ^{13}C NMR spectra of compounds **3** and **4** exhibited resonances due to aliphatic protons and carbons. For compound **3**, a proton singlet at δ 3.86 (2H), a carbon resonance at δ 37.3, and a molecular ion at *m*/*z* 470[5] led to its identification as the known 1,2,3,4-tetraphenylfluorene.[6,7] Precise mass data for **4** gave the formula $C_{44}H_{32}$,[8] showing that it retains all the carbons from **1**, but that two hydrogens have been added. The AMX system (3H) in its ^1H NMR spectrum and the presence of two aliphatic carbon resonances (δ 38.4 and 49.2) strongly suggest that this material is 9-benzyl-1,2,3,4-tetraphenylfluorene.[8] The structure of **5** was not immediately apparent from its spectral characteristics. Its ^1H NMR spectrum contains only complex and overlapping aromatic resonances, but a precise mass measurement gave the formula $C_{44}H_{28}$.[9] Fortunately, a single crystal of **5** was obtained, and X-ray analysis[10] showed it to be 1,2,3,8-tetraphenylbenz[*e*]acephenanthrylene (Fig. 1), which results from a double cyclization and dehydrogenation of **1**.

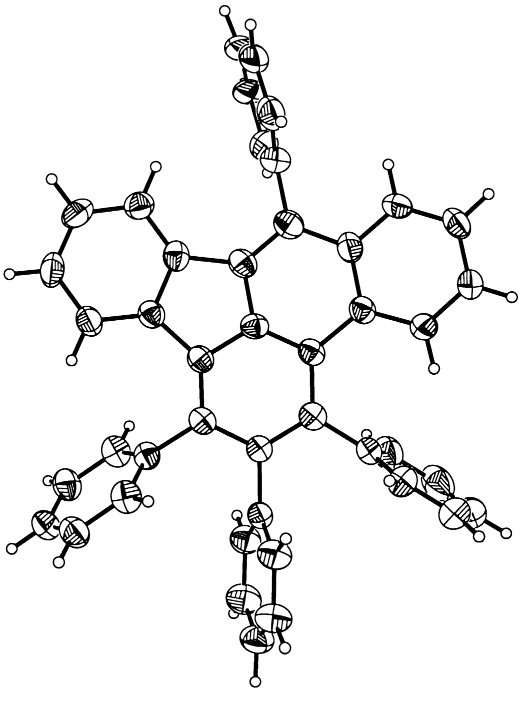


Figure 1. X-Ray structure of 1,2,3,8-tetraphenylbenz[*e*]acephenanthrylene (**5**). Thermal ellipsoids are drawn at the 50% probability level

The cleavage of alkyne **1** to yield **3** is most surprising; we know of no comparable cobalt-catalyzed reaction. It seems extremely unlikely that arylcarbynes could have been formed by the direct insertion of cobalt into the alkyne, although such species might have led to the observed products. Instead, we propose the following speculative mechanistic scheme (Fig. 2). The identity of the active cobalt species is unknown, but it may be multinuclear, and so it is indicated merely as 'Co_nL_m'. After an initial activation of **1** by cobalt complexation and *ortho* metallation, a migratory insertion into one of the phenyl C–H bonds would yield the fluorene nucleus, perhaps as part of a complex such as **6**. A similar insertion into a second phenyl group would lead to the minor product **5**, but a hydride shift would give the carbene **7**, and reduction or hydrolysis of **7** would yield the benzyl fluorene **4**. More difficult to explain is the production of the major product **3**, which must involve some type of σ-bond activation. Perhaps it forms by cobalt insertion into the olefin of **8**, followed by reduction of the metal fluorenylidene **9**. Alternatively, under such rigorous reaction conditions the weak, doubly-benzylic bond in **7** might fragment, and the resulting radical **13** could scavenge hydrogen from the solvent to yield **3**.

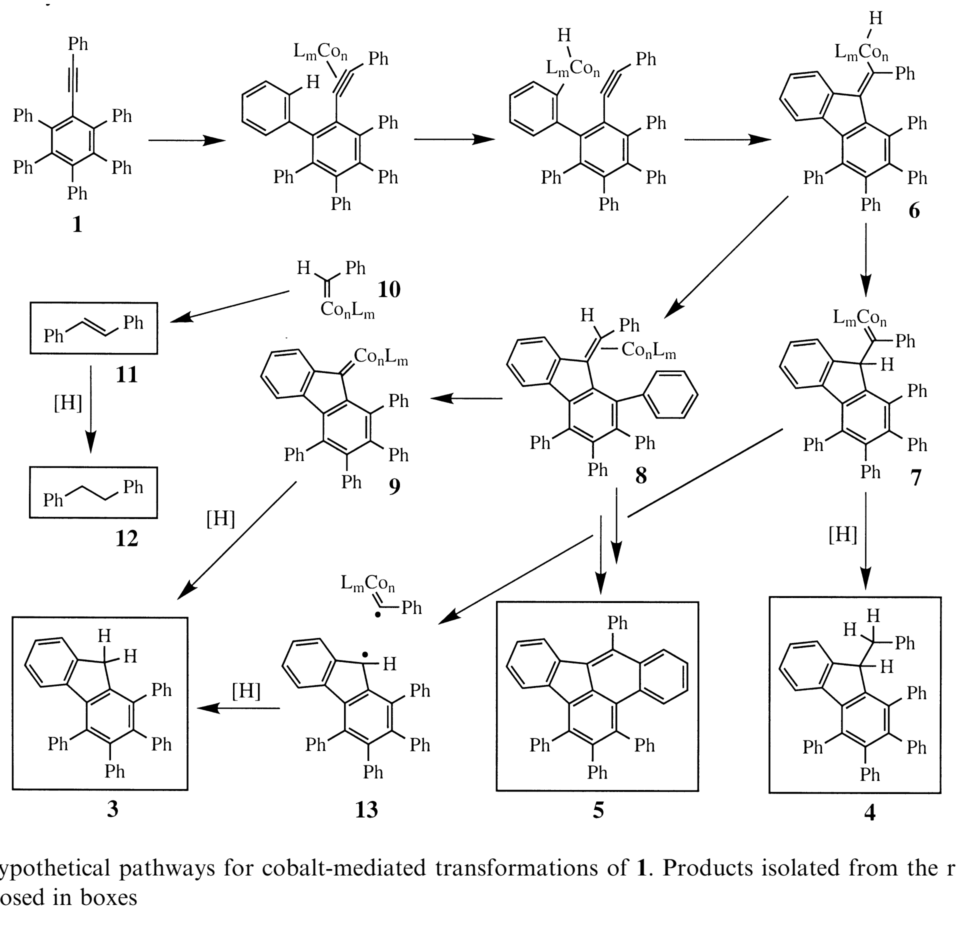


Figure 2. Hypothetical pathways for cobalt-mediated transformations of **1**. Products isolated from the reaction mixture are enclosed in boxes

The existence of metal carbenes in this reaction is supported by the finding of various alkene metathesis products. A very nonpolar fraction (38 mg) was composed primarily of *trans*-stilbene (**11**) and 1,2-diphenylethane (**12**) (*cis*-stilbene was not observed). These small organics were not present in sufficient quantity to account for all of the ‘lost’ seven-carbon fragments; however, it is clear that some hydrogenation is occurring in this reaction mixture, and so it is likely that small carbenes such as **10** would simply be reduced to toluene, just as the carbenes **7** and **9** would be reduced to the observed **3** and **4**. Whatever the mechanism of formation of **3**, it is remarkable that such a C–C cleavage route is more than competitive with the simpler cyclization reactions occurring in this reaction.

Acknowledgements

This work was supported by NSF Grant CHE-9707958 which is gratefully acknowledged. We thank S. C. Lee for helpful discussions.

References

1. Tong, L.; Ho, D. M.; Vogelaar, N. J.; Schutt, C. E.; Pascal Jr., R. A. *J. Am. Chem. Soc.* **1997**, *119*, 7291–7302.
2. Dilthey, W.; Schommer, W.; Höschen, W.; Dierichs, H. *Ber.* **1935**, *68*, 1159–1162.
3. Rausch, M. D.; Tokas, E. F.; Mintz, E. A.; Clearfield, A.; Mangion, M.; Bernal, I. *J. Organomet. Chem.* **1979**, *172*, 109–131.
4. Rausch, M. D.; Westover, G. F.; Mintz, E.; Reisner, G. M.; Bernal, I.; Clearfield, A.; Troup, J. M. *Inorg. Chem.* **1979**, *18*, 2605–2615.
5. For **3**: mp 237–240°C [lit.[6] 246°C, lit.[7] 225–226°C]; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 3.86 (s, 2H), 6.43 (d, J = 8 Hz, 1H), 6.89 (m, 10H), 7.02 (t, J = 8 Hz, 1H), 7.20 (t, J = 8 Hz, 1H), 7.27 (m, 10H), 7.45 (d, J = 8 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 37.3, 123.1, 124.5, 125.28, 125.31, 126.26, 126.28, 126.35, 126.5, 126.6, 126.7, 127.8, 128.0, 129.9, 130.2, 131.40, 131.42, 135.9, 137.8, 138.4, 139.1, 139.8, 140.0, 140.1, 140.2, 140.6, 141.70, 141.73, 144.1 (29 of 29 expected peaks observed); FAB MS, *m/z* 470 (M$^+$, 100).
6. Ghosh, K.; Bhattacharya, A. J. *Indian J. Chem.* **1977**, *15B*, 32–35.
7. Sengupta, S. C.; Mitra, A. *J. Indian Chem. Soc.* **1959**, *36*, 825–829.
8. For **4**: mp 273–274°C; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 2.03 (dd, J = 13, 10 Hz, 1H), 3.00 (dd, J = 13, 3 Hz, 1H), 4.38 (dd, J = 10, 3 Hz, 1H), 6.19 (d, J = 8 Hz, 1H), 6.55 (d, J = 8 Hz, 1H), 6.64 (m, 3H), 6.83 (m, 12H), 6.99 (t, J = 8 Hz, 1H), 7.11 (m, 7H), 7.27 (t, J = 8 Hz, 1H), 7.32 (d, J = 8 Hz, 1H), 7.44 (t, J = 8 Hz, 1H), 7.64 (d, J = 8 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 38.4, 49.2, 123.2, 125.0, 125.5, 126.1, 126.2, 126.4, 126.6, 126.8, 126.9, 127.7, 128.1, 128.4, 129.7, 129.9, 130.0, 130.9, 131.1, 131.4, 131.5, 131.7, 132.1, 136.2, 137.8, 138.1, 139.7, 140.1, 140.2, 140.4, 141.1, 145.2, 147.9 (33 of 34 expected peaks observed); MS, *m/z* 600 (M$^+$, 100); HRMS: 560.2499; calcd for $C_{44}H_{32}$: 560.2504.
9. For **5**: mp > 400°C; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 6.4–7.7 (m); MS, *m/z* 556 (M$^+$, 100); HRMS: 556.2196; calcd for $C_{44}H_{28}$: 556.2191.
10. A crystal of **5** measuring 0.43×0.30×0.04 mm was used for X-ray measurements. Crystal data: $C_{44}H_{28}$; triclinic, space group $P\bar{1}$ (No. 2); $a = 9.8213$ (4) Å, $b = 12.1285$ (7) Å, $c = 13.6158$ (7) Å, $\alpha = 64.967$ (2)°, $\beta = 86.852$ (3)°, $\gamma = 83.841$ (3)°, $V = 1461.0$ (1) Å^3, $Z = 2$, $D_{\text{calcd}} = 1.265$ g/cm^3. MoKα radiation ($\lambda = 0.71073$ Å) was employed for data collection ($\theta_{\text{max}} = 22.44°$) at 200 K on a Nonius KappaCCD diffractometer. A total of 9046 reflections were indexed, integrated, and corrected for Lorentz and polarization effects by using the program DENZO,[11] and then were merged to 3783 unique reflections ($R_{\text{int}} = 0.036$) by using SCALEPACK.[11] The structure was solved by direct methods (SHELXTL[12]) and refined by full-matrix least-squares on F^2. The molecule is disordered over two positions in an 83:17 ratio; this disorder is evident only for the benz[*e*]acephenanthrylene core and the C(8)-phenyl group. In the final crystallographic model, all carbons of the major component were refined anisotropically, with hydrogens riding [C–H = 0.95 Å, $U(\text{H}) = 1.2U(\text{C})$]; the minor component was refined isotropically as two rigid bodies with light restraints on the thermal parameters. The refinement converged to $R(F) = 0.050$, $wR(F^2) = 0.117$, and $S = 1.10$ for 2842 reflections with $F > 4\sigma(F)$, and $R(F) = 0.075$, $wR(F^2) = 0.130$, and $S = 1.04$ for 3783 unique reflections, 437 variables, and 30 restraints.
11. Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307–326.
12. Sheldrick, G. M. SHELXTL Version 5; Siemens Analytical X-ray Instruments: Madison, Wisconsin, 1996.